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14. ABSTRACT

This report describes the first phase of a long-term program aimed at establishing a facility that can address protective coatings research needs of the Department of Defense using the latest in combinatorial materials chemistry high-throughput discovery and evaluation methodology. The protective coatings application being addressed is environmentally compliant antifouling and fouling release coating for Navy ships. The objectives of Phase I were to: (1) initiate research on novel antifouling and fouling release coatings, and (2) develop and implement a facility for combinatorial high throughput experimentation for polymer materials and marine coating design, development, and evaluation. Both objectives were accomplished. The first groups of coatings, containing novel bound biocides on a silicone backbone and prepared through conventional synthesis methods, had several formulations that gave promising results during tests at ONR-supported test sites. A facility, unique among U.S. universities, was designed in renovated laboratory space and staffed with engineers and scientists, and more than $2,400,000 worth of patented equipment and software were procured from the leading vendor of combinatorial high throughput experimentation systems, installed and qualified.

15. SUBJECT TERMS

Combinatorial chemistry; high throughput experimentation, silicones; antifouling coatings, fouling release coatings.

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Advanced Marine Coatings for Naval Vessels – Phase I. Antifouling and Fouling Release Coatings

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FINAL REPORT

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30 September 2003

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Final Report: Advanced Marine Coatings for Naval Vessels.
Phase I. Antifouling and Fouling Release Coatings

Abstract

This report describes the first phase of a long-term program aimed at establishing a facility that can address protective coatings research needs of the Department of Defense using the latest in combinatorial materials chemistry high-throughput discovery and evaluation methodology. The protective coatings application being addressed is environmentally compliant antifouling and fouling release coating for Navy ships. The objectives of Phase I were to: (1) initiate research on novel antifouling and fouling release coatings, and (2) develop and implement a facility for combinatorial high throughput experimentation for polymer materials and marine coating design, development, and evaluation. Both objectives were accomplished. The first groups of coatings, containing novel bound biocides on a silicone backbone and prepared through conventional synthesis methods, had several formulations that gave promising results during tests at ONR-supported test sites. A facility, unique among U.S. universities, was designed in renovated laboratory space and staffed with engineers and scientists, and more than $2,400,000 worth of patented equipment and software were procured from the leading vendor of combinatorial high throughput experimentation systems, installed and qualified.

1.0 Introduction and Objectives

North Dakota State University has embarked on a multi-year program aimed at establishing a facility that can address protective coatings research needs of the Department of Defense using the latest in combinatorial materials chemistry high-throughput discovery and evaluation methodology. The program is a partnership of NDSU's new Center for Nanoscale Science and Engineering (CNSE), and Department of Polymers and Coatings (P&C), which has a 100-year history of polymer-based protective coatings research. This report describes the first phase of work, which had as it *goal*: to develop the facility and begin research on the first protective coatings application, protection of Navy ships from marine life that can foul their hulls, thereby reducing speed and maneuverability and increasing fuel usage. The protective coatings developed here could also be applicable in the many environments where biota foul engineered structures in aquatic environments and in other fabricated materials that contact potentially harmful biological life.

Our *objectives* for Phase I were to: (1) initiate research on environmentally compliant antifouling and fouling release coatings, and (2) develop and implement a facility for combinatorial high throughput methods for polymer materials and marine coating design, development, and evaluation. Both objectives were accomplished. The first groups of coatings, prepared through conventional synthesis methods, had several formulations that gave promising results during the first short-term tests at ONR-supported test sites. A facility, unique among U.S. universities, was designed in renovated laboratory space and staffed with engineers and scientists, and more than $2,400,000 worth of patented equipment and software were procured from the leading vendor of combinatorial high throughput experimentation systems.

2.0   Technical Approach

The technical approach involves both the synthesis of novel polymer systems for antifouling and foul release coatings as well as developing novel methods for rapidly preparing and screening thousands of compositions.

Several design strategies are being evaluated for the novel polymer systems. The first is a synthetic approach which simultaneously imparts antifouling and foul release characteristics to a single coating system. Unique functional siloxane oligomers are being prepared that have bound biocides, "textural" groups (e.g. hydrophobic or hydrophilic), as well as reactive (cross-linking) functional groups. We are comparing coating systems in which all of these functionalities are attached to a single polymer resin with coating systems in which the functionalities are attached to different polymers and then physically blended. The current focus is on incorporation of bacterial biocides which are approved by the U.S. EPA for industrial use. In many cases, the metabolic mechanism of action for biocidal agents (e.g. uptake vs. external contact) is unclear, thus variations in the method of biocide attachment (e.g. strong or weak bonds) as well as functional group concentration and distribution are being evaluated. If coating surfaces that are truly biocidal toward bacterial fouling are developed, this may lead to an understanding of the relationship between micro-fouling and macro-fouling in the marine environment.

Simultaneously a second approach to durable foul release coatings, which builds on prior efforts, is being pursued. Siloxane-polyurethane coating systems are being synthesized that self-stratify into a soft siloxane layer over a more durable cross-linked polyurethane coating. Cross-linking the coatings will provide a stable surface that does not undergo reorganization when exposed to seawater.

These coating systems are extremely complex. There are no a priori models that predict which composition will have the best balance of performance properties. In order to be able to evaluate all of the possible structural and compositional variants of these approaches, combinatorial and high throughput methods for synthesis, sample preparation and screening of key properties are being implemented.

3.0 Results and Discussion

3.1 Design, synthesis, characterization, and biological challenge of multi-functional silicone resins for use in coating applications.

Personnel: Thomas Ready and Seok-Bong Choi (Senior Research Scientists), Philip Boudjouk (VP-Research, Creative Activities, & Technology Transfer), and Johnson Thomas (Postdoctoral Fellow). Renae Feldjheim and Daniel Rhomas (Undergraduate Research Assistants).

We have modified commercially available poly(methylhydrosiloxane) and poly(dimethyl-co-methylhydro-siloxane) by grafting organic biocide, cross-linking groups and pendant hydrophilic or hydrophobic groups onto the silicone backbone. Biocides used were 2,4,4'-trichloro-2'-hydroxydiphenyl ether (common name: Triclosan, also known as Irgaguard B 1000, Ciba Corp.) and vinyl pyridinium moieties (EPA approved for industrial use). Biocide attachment was achieved either by hydrosilation, which produces a hydrolytically stable Si-C linkage or by dehydrogenative coupling, which produces a Si-O-C linkage, which may allow slow hydrolytic release. The different silicone resins synthesized are given below.

Resin 1. Attachment of epoxy cross-linking moiety onto poly(methylhydrosiloxane).
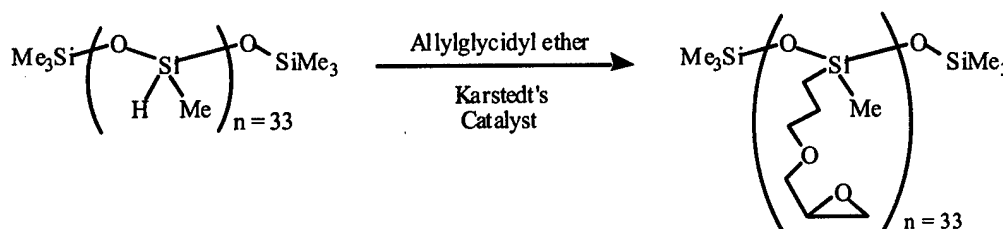
The glycidyl ether cross-linking moiety was grafted onto the silicone backbone by reacting allylglycidyl ether with poly(methylhydrosiloxane) in the presence of Karstedt's catalyst in toluene at 90 °C. Completion of this reaction was monitored by NMR. The product resin was a clear liquid and was obtained in a yield of 98%. Coatings made from this resin will serve as internal reference coatings.

Resin 2. Attachment of biocide onto cyclic methylhydrosiloxane.

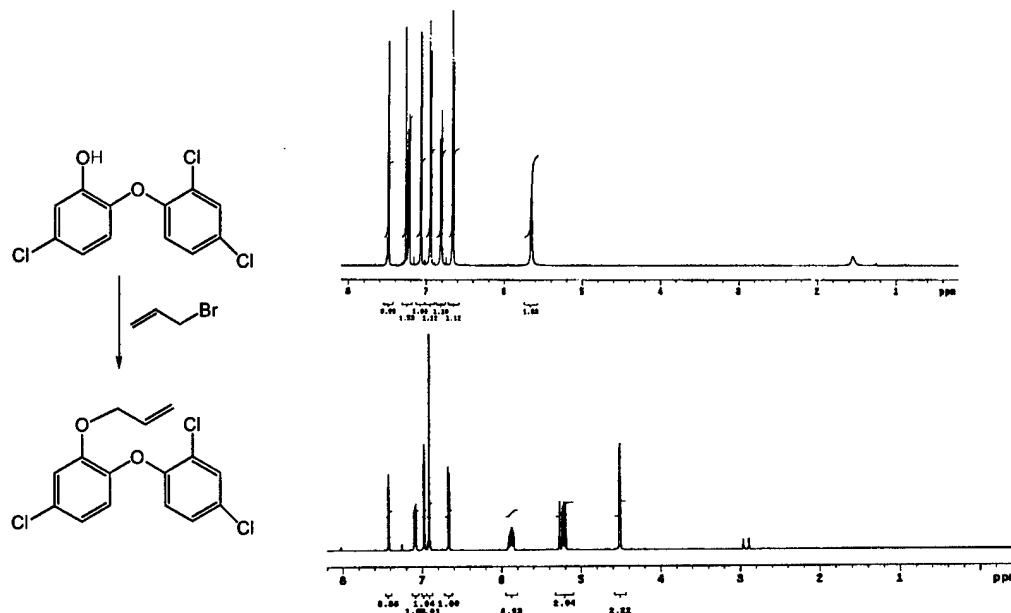Triclosan (Irgaguard B1000, Ciba) was modified to incorporate an allyl functionality (Figure 1)

Figure 1.
Modification of Triclosan to Incorporate Allyl Functionality

The allyl biocide was introduced into the cyclic methylhydrosiloxane backbone using Karstedt's catalyst in toluene at 90 °C. The completion of this reaction was monitored by NMR. The yield of the reaction was as high as 98% and the resin was clear liquid. The mole percentage of allyl biocide within polymer backbone is around 25 %.
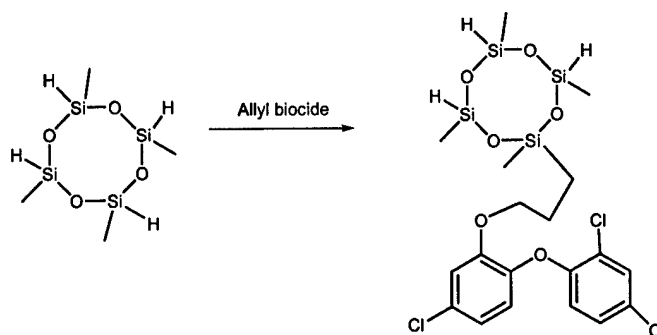
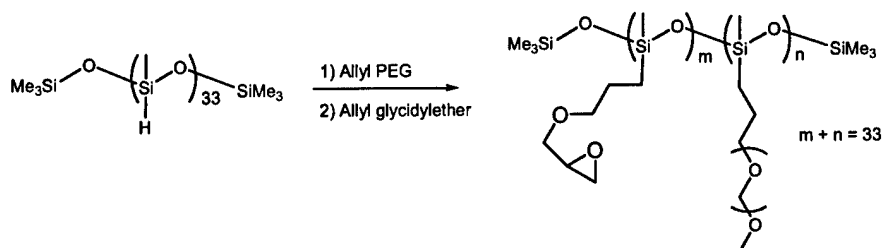**Resin 3.** Attachment of biocide moiety and epoxy cross-linking groups onto cyclic methyl hydrosiloxane.

The allyl-Trichlosan biocide was introduced into the cyclic methylhydrosiloxane backbone using Karstedt's catalyst in toluene at 90 °C. The completion of this reaction was monitored by NMR.

This was followed by the addition of allyl glycidyl ether and the incorporation of the glycidyl group was also confirmed by NMR. The yield of the reaction was as high as 98% and the resin was clear liquid. The mole percentage of allyl biocide and glycidyl ether within the polymer backbone is 25% and 75 % each.
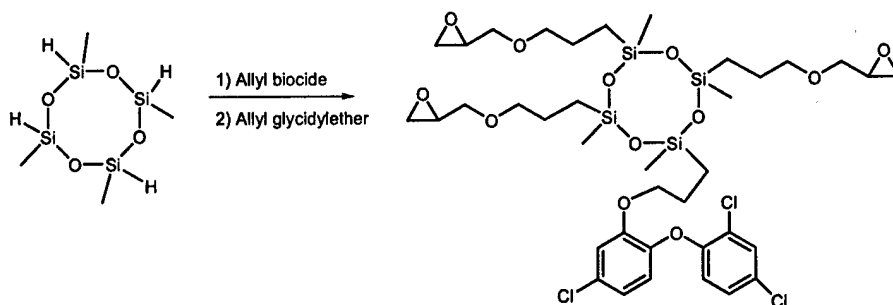

Resin 4. Attachment of hydrophilic Polyethylene glycol moiety and epoxy cross-linking group onto poly(methylhydrosiloxane).

Polyethylene glycol monomethyl ether was first converted to allyl polyethylene glycol monomethyl ether. This allyl modified PEG was introduced into the poly(methyl hydrosiloxane) backbone using Karstedt's catalyst in toluene at 90 °C . The completion of this reaction was monitored by NMR. This was followed by the addition of allyl glycidyl ether and NMR also confirmed the incorporation of the glycidyl group. The yield of the reaction was as high as 98% and the resin was clear liquid. The mole percentage of allyl PEG and glycidyl ether within polymer backbone is around 50 % each.


Resin 5. Attachment of biocide, hydrophilic Polyethylene glycol moiety and epoxy cross-linking groups onto the poly(methylhydrosiloxane).

The ally-Trichlosan biocide was incorporated into the poly(methylhydrosiloxane) backbone followed by allyl polyethylene methyl ether and allyl glycidyl ether using Karstedt's catalyst in toluene at 90 °C. Incorporation of all the pendant groups were confirmed by proton NMR and the yield was 96%. The resulting resin was clear liquid. The ratio for m/n/p is 2:1:1.
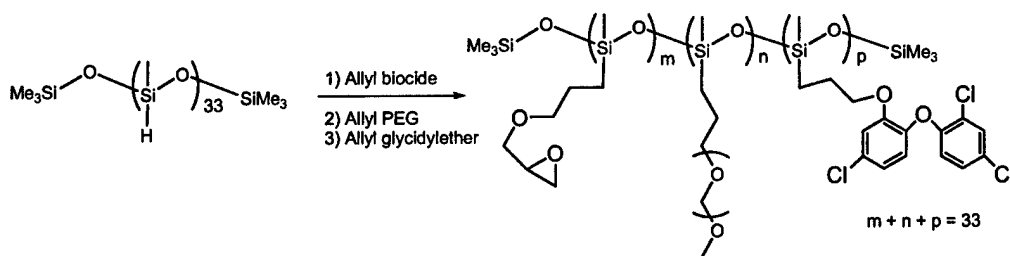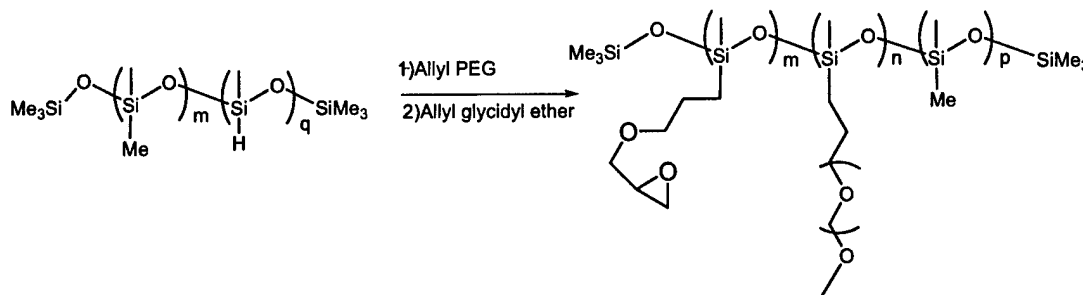
Resin 6. Attachment of biocide and epoxy cross-linking groups onto poly(dimethyl-co-methyl hydro-siloxane) backbone.

Allyl-Trichlosan biocide and allyl glycidyl ether were incorporated in the same fashion as described in the previous cases into poly(dimethyl-co-methylhydrosiloxane) backbone and was characterized by ^{1}H NMR. The yield of this reaction was 96% and the resin was clear liquid. The ratio for m/n/p is 2:1:1.
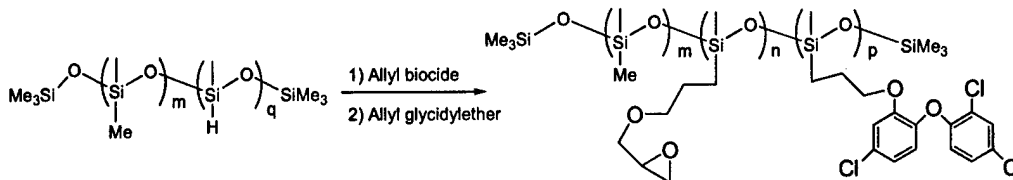
Resin 7. Attachment of Polyethylene glycol and epoxy cross-linking groups onto poly(dimethyl-co-methyl hydro-siloxane) backbone.

PEG was introduced into the co-polymer backbone via hydrosilylation followed by glycidyl ether for cross linking. NMR showed quantitative incorporation of these groups. The reaction yielded a clear resin with >95% yield. The ratio for m/n/p is 1:1:2.

Resin 8. Attachment of hydrophobic perfluoro decane and cross-linking groups onto poly(dimethyl-co-methyl hydro-siloxane) backbone.

The perfluro and epoxy cross-linking groups were introduced via hydrosilylation and the product was characterized via ^{1}H NMR and this reaction yielded clear resin with more than 95% yield. The ratio for m/n/p is 1:1:2.
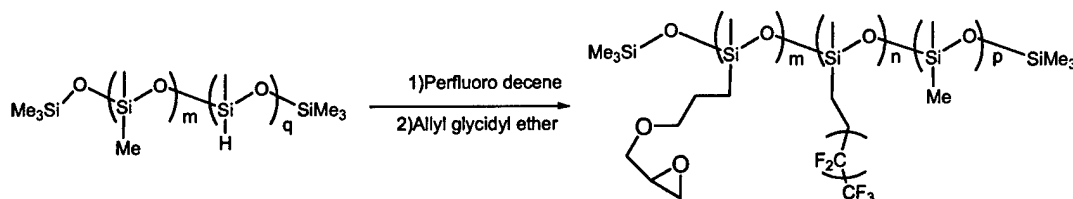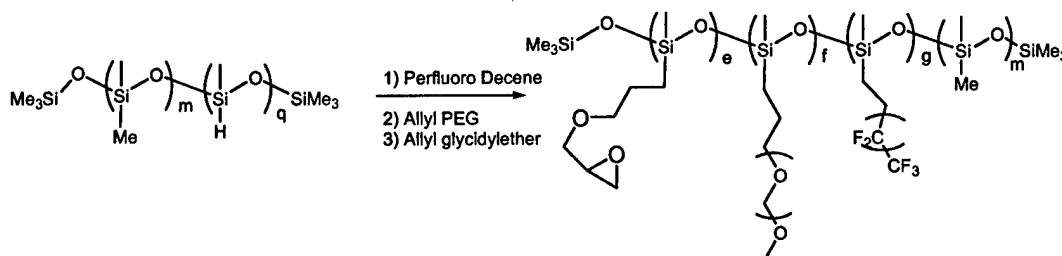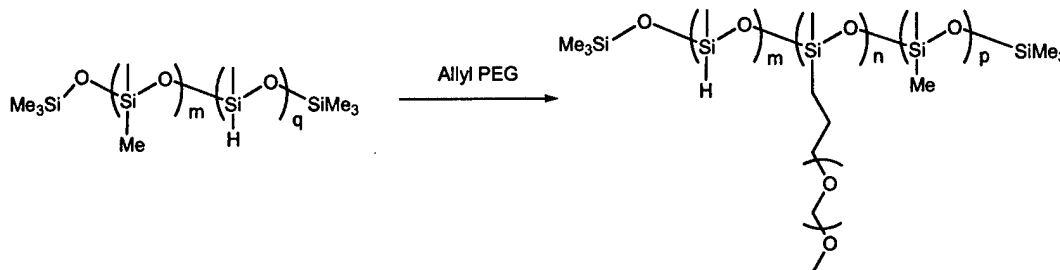
Resin 9. Attachment of hydrophobic Perfluoro decane, hydrophilic Polyethylene glycol, and epoxy cross-linking groups into poly(dimethyl-co-methyl hydro-siloxane) backbone.

This resin was prepared by the incorporation of a hydrophilic, hydrophobic and the cross-linking moieties into the copolymer backbone via hydrosilylation. ^{1}H NMR showed the incorporation of all the three groups and the yield was above 90% and the reaction yielded a slight yellow resin. The mole ratio for e:f:g:m is 2:1:1:4.

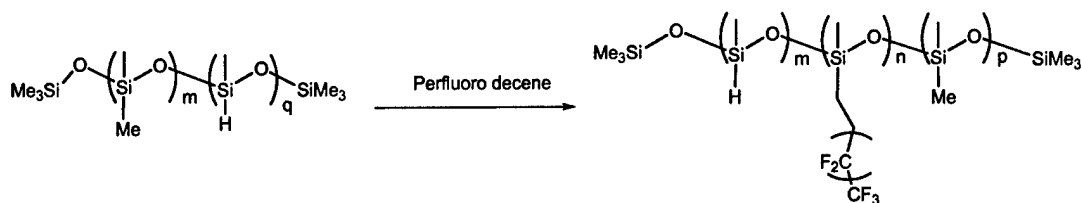**Resin 10.** Attachment of hydrophilic Polyethylene glycol moiety onto poly(dimethyl-co-methylhydro-siloxane) backbone.

This resin was prepared by the incorporation of only PEG and was cross-linked through the residual hydrogen in the backbone. The mole ratio for m:n:p is 1:1:2.

Resin 11. Attachment of hydrophobic perfluorodecane moiety onto poly(dimethyl-co-methyl hydro-siloxane) backbone.

As discussed above this resin was prepared with the objective of cross-linking through the H atom in the copolymer backbone. The mole ratio for m:n:p is 1:1:2.


Resin 12. Incorporation of hydrophobic perfluorodecane and PEG into poly(dimethyl-co-methyl hydro-siloxane) backbone.

This resin was prepared as a way of modifying the hydrophilic and hydrophobic characteristics in the eventual coating. The procedure adopted was same as above. The mole ratio for m:n:p:q is 2:1:1:4.
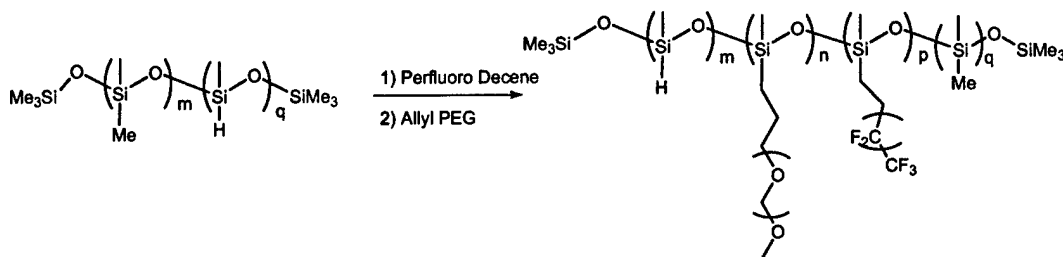
Resin 13. Attachment of pyridinium biocide (alkyl attachment) and epoxy cross-linking moieties onto the poly(methylhydrosiloxane) backbone.

A stoichiometric amount (50 mole %) of allyl glycidyl ether was reacted with poly(methyl-hydrosiloxane) using Karstedt's catalyst in toluene at 90 C. After all of the allyl functionality was reacted (monitored by NMR), a stoichiometric amount (50 mol %) of vinylpyridine and additional catalyst were introduced into the reaction mixture. Incorporation of all the pendant groups were confirmed by proton NMR and the yield was 94%. An excess of ethylbromide of (1.1 ethylbromide / 1.0 pyridine moiety) was introduced to the reaction mixture and warmed to 40° C. The resin was isolated as a brown viscous semi-solid.
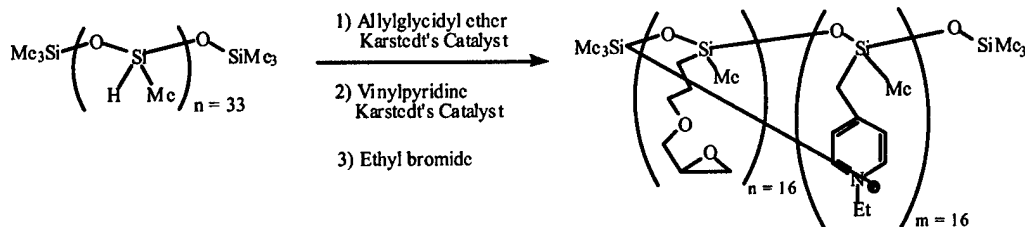

Resin 14. Attachment of pyridinium biocide (alkoxy attachment) and epoxy cross-linking moieties onto the poly(methylhydrosiloxane) backbone.

A stoichiometric amount (50 mole %) of allyl glycidyl ether was reacted with poly(methylhydrosiloxane) using Karstedt's catalyst in toluene at 90 C. After all of the allyl functionality was reacted (monitored by NMR), a stoichiometric amount (50 mol %) of 4-pyridinepropanol and Wilkinson's catalyst were introduced into the reaction mixture. Incorporation of all the pendant groups were confirmed by proton NMR and the yield was 96%. An excess of ethylbromide of (1.1 ethylbromide / 1.0 pyridine moiety) was introduced to the reaction mixture and warmed to 40° C. The resin was isolated as a brown viscous semi-solid.
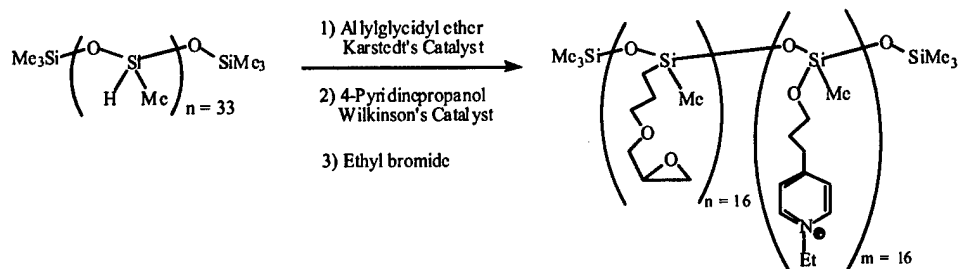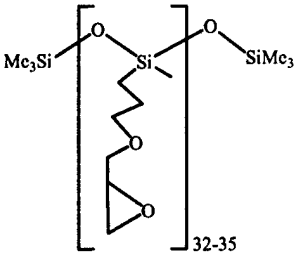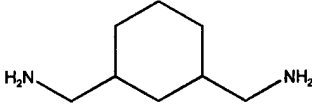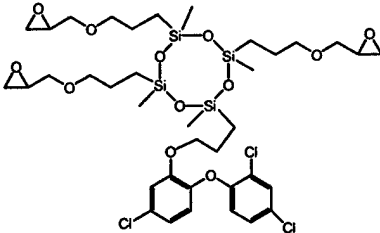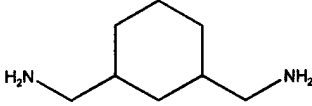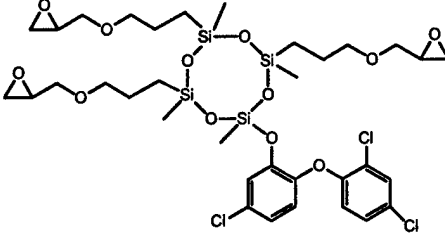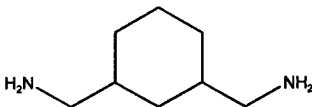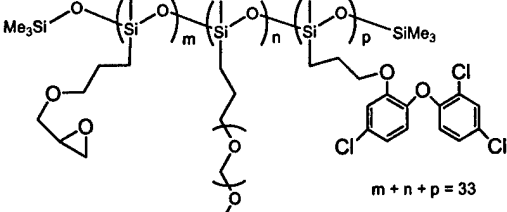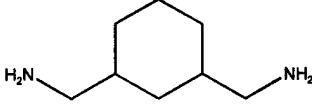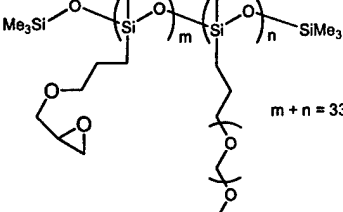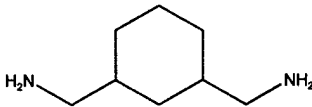

Coating Synthesis: The modified silicone resins were used to prepare various coatings using one of two types of cross-linking agents. Silicones containing the glycidyl ether group were cross-linked with 1, 3-cyclohexanebis(methylamine) (**1**). Silicones with hydrosilyl groups with divinyl terminated poly(dimethylsiloxane) (**2**). Coatings made of these materials are being evaluated to determine the effect of different variables such as biocide loading, cross-link density and the nature of cross-linking type on antifouling/fouling release properties.
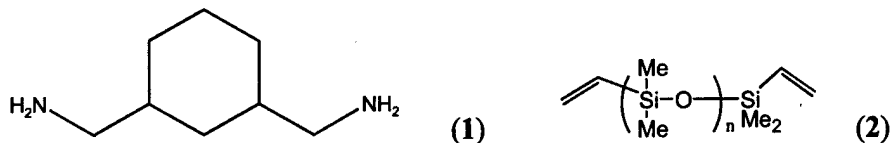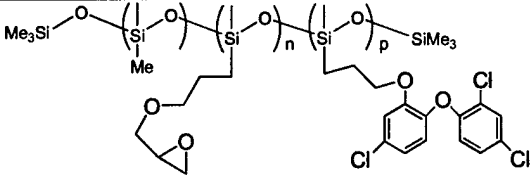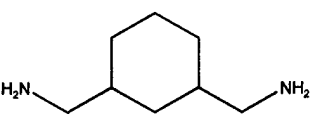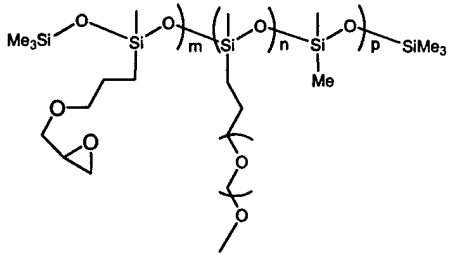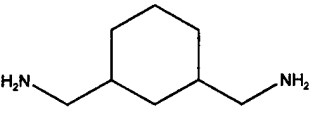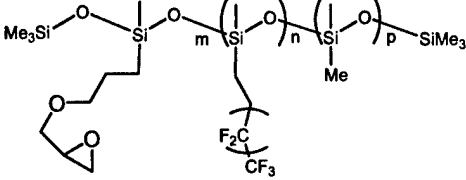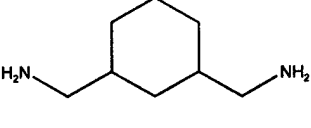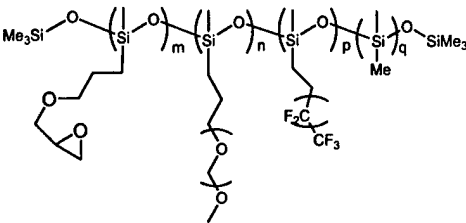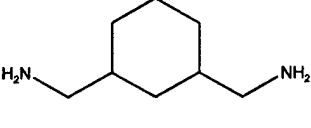
For coating formulations made using the diamine cross-linker (**1**), stoichiometric amounts (1 epoxy equivalent = 1 amine equivalent or NH functionality) of the curing agent were added to the epoxy silicone resin and thoroughly mixed. These coating formulations typically had a pot-life of 60 minutes. Coatings were applied to glass slides as well as aluminum panels and the samples were kept at the ambient temperature for 3h and further at 60 °C for 1h. The coatings produced were characterized by contact angle measurements, DSC, TGA and profilometry.

Silicone resins containing unreacted silicon-hydride bonds were cured by divinyl-terminated poly(dimethylsiloxane) (**2**) by mixing in stoichiometric amounts (1Si-H to 1 vinyl functionality) and applied to glass slides and aluminum panels where they were kept at ambient temperature for 24h and then were further cured at 80 °C for 6h.These resins were clear in appearance and had a long pot life of 24h. The coatings were characterized by contact angle measurements, DSC, TGA and profilometry.

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Table 1: Coating samples prepared.

Coatings	Resin	Cross linker
I		
II		
III		
IV		
V		

VI		
VII		
VIII		
IX		
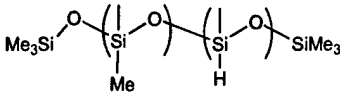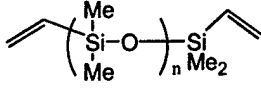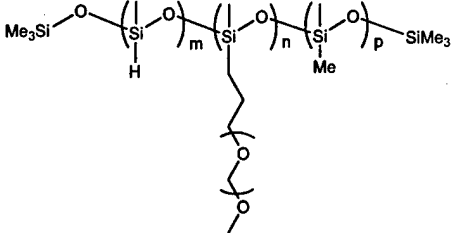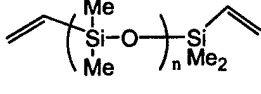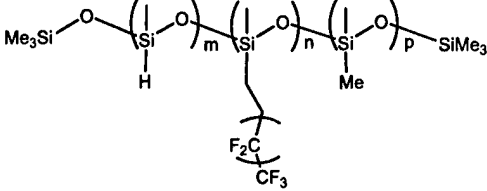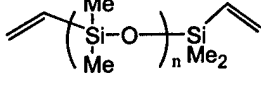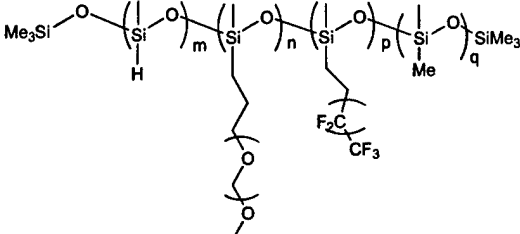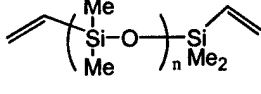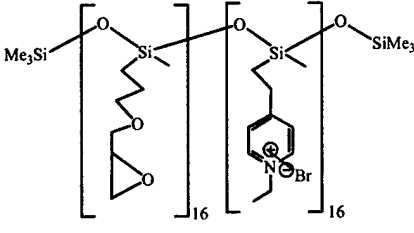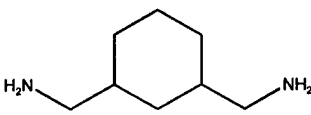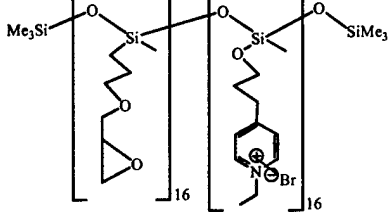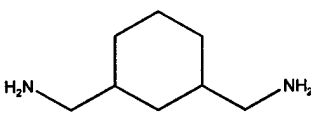
X		
XI		
XII		
XIII		
XIV		
XV		

Table 2. Static Contact Angle Measurements.

Coating	Contact Angle (H_2O)	Surface Energy
I	83.5	34.95[*]
II	92	29.4
III	76	39.5
IV	74	40.5
V	Failed	
VI	100	25
VII	89	31.2
VIII	95	27.6
IX	85	33.5
X	112	18.2
XI	95	27.2
XII	110	19.2
XIII	103	22.8

[*] Measurement (avg. of 24) obtained using Symyx combinatorial tool

Contact angle measurements were done on FTA125 Dynamic Contact Angle Analyzer shows interesting results or using the Symyx combinatorial contact angle measurement tool. Coatings containing heteroatoms and cured using the amine curing agent showed lower contact angle values (coatings II, III, IV, VI, VII, VIII, IX) compared to coatings cured with the divinyl-terminated poly(dimethylsiloxane). Coatings derived from cyclic siloxane and poly(methylhydrosiloxane) (I, II, & III) exhibited lower contact angle values compared to the coatings containing poly(dimethylsiloxane)-co-poly(methylhydro-siloxane) copolymer. The presence of dimethylsiloxane segments in these systems renders these coatings more hydrophobic. Contact angle measurements on these coatings are in progress.

Thermal analysis. Thermogravimetric analyses were carried out on Perkin Elmer TGA 7 instrument. Samples were heated from ambient to 600°C at 20 °C/ min. Degradation temperature of coatings cured by the diamine shows significantly higher degradation temperature (>300 °C) compared to the coatings cured by divinyl siloxane (150 °C).

DSC measurements were carried out using TA instrument Q1000 series from -90 °C to +100 °C at a heating rate of 10 °C/min. The samples were subjected to three heating and cooling cycles and the data from the third cycle is taken. The glass transition temperature of the amine cured samples is significantly higher (-12 °C to +10 °C) compared to the divinyl siloxane cured ones (-48 °C). In the case of amine cured coatings, Cyclic siloxane shows higher Tg (+ 17 °C) compared to the poly(hydromethyl)-co-poly(dimethyl-siloxane) copolymer (-12 °C). Some representative DSC plots are given below.
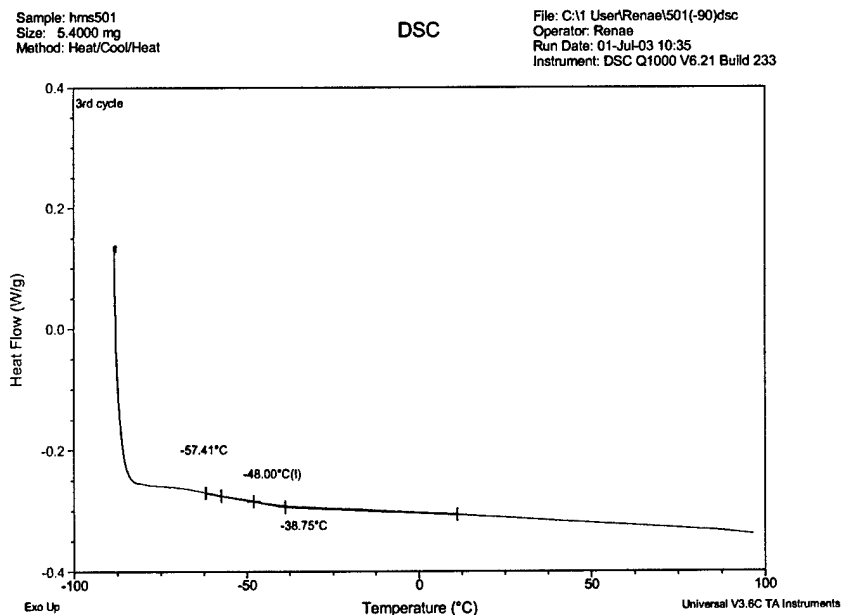
Figure 1. DSC plot for coating IX.
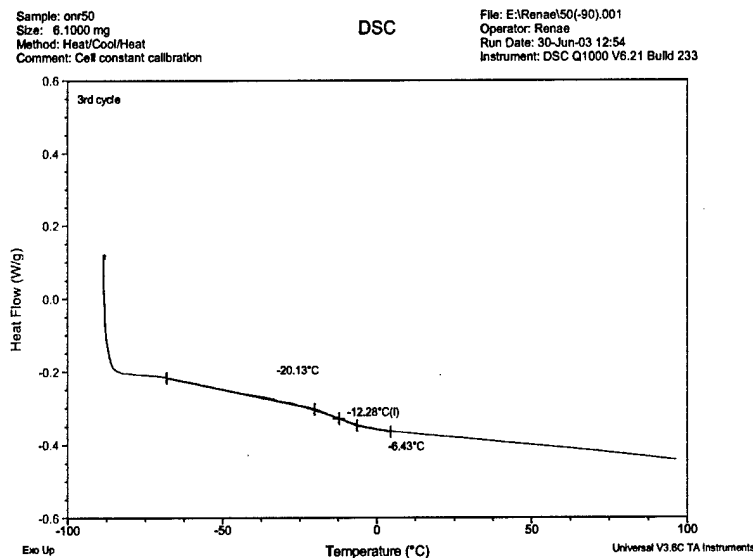
Figure 2. DSC plot for coating V.
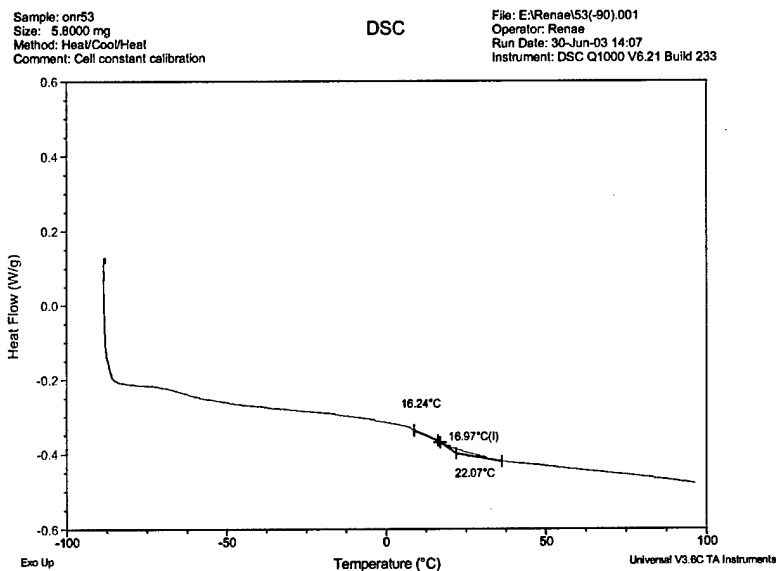
Figure 3. DSC plot for coating II.

Biological Challenge of NDSU Coatings

Coatings I, II, III, IV, VI, and X were submitted to Florida Institute of Technology (Swain Laboratory), University of Birmingham, UK (Callow Laboratory), and the University of Hawaii

(Smith Laboratory) for laboratory/ field tests. The various testing sites require somewhat different formats for coating evaluation.

NDSU is also interested in establishing a new substrate format for testing at each of the facilities above. In conjunction with NDSU's Combinatorial High Throughput Facility work flow, establishment of a coating array as a viable format at these test facilities would enhance the volume of coating types which could be screened while using essentially the same amount resources. Experiments were performed to validate the efficacy of biological challenges (either *in vitro* assays or field immersion testing) on our "coating array" format. To all three testing sites, we submitted four (4) 4" x 8" panels, which had 12 coating patches on each of them (see Figure 1). In the future, each "patch" might be a different coating type, but for this experiment all of the "patches" were of the same coating type, identical in composition to a singular coating type present in the first experiment (the reference coating will also be included in the first experiment). The dimensions of the coating patches probably preclude any meaningful results to be obtained from full macro-fouling immersion testing, but it is hoped that they will lend themselves to studying *early* settlement of fouling. Specifically, we have sought to obtain a statistical analysis of the differences in *early* fouling settlement between our 4" x 8" coating array format and fully coated 4" x 8" panels.

Florida Institute of Technology (Preliminary Barnacle SettlementTesting)

Four replicates of each type of coating type (or array type) were submitted for field immersion testing. Coatings (I, II, III, IV, VI, and X) were applied on top of 4" x 8" aluminum substrates previously coated with Sherwin Williams Macro-poxy 646 primer.

Two sets of coating array formats were submitted: (1) 12 Coating array "patches" of Coating I were applied on top of 4" x 8" aluminum 5005 H24 substrates previously coated with Sherwin Williams Macro-poxy 646 primer (see Figure 4), and (2) 12 Coating array "patches" of Coating I were applied on top of 4" x 8" aluminum 5005 H24 substrates previously coated with Sherwin Williams Macro-poxy 646 primer Interlux Trilux Prop & Drive top-coat (copper containing anti-fouling paint).

Panels were placed back to back and arranged on a test rack which was lowered into the water. Hence, two of the replicates of each coating type were facing East in the water and two replicates each coating type were facing West in the water. Preliminary results discussed here are based on a total immersion time of 20 days (June 3 – June 23, 2003).

Barnacle settlement counts were assessed using digital photographs taken on June 23, 2003. Foul-release data was not obtained or transmitted.
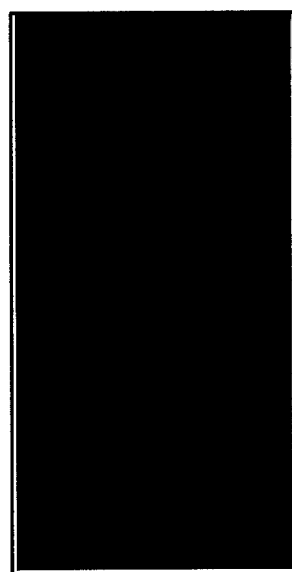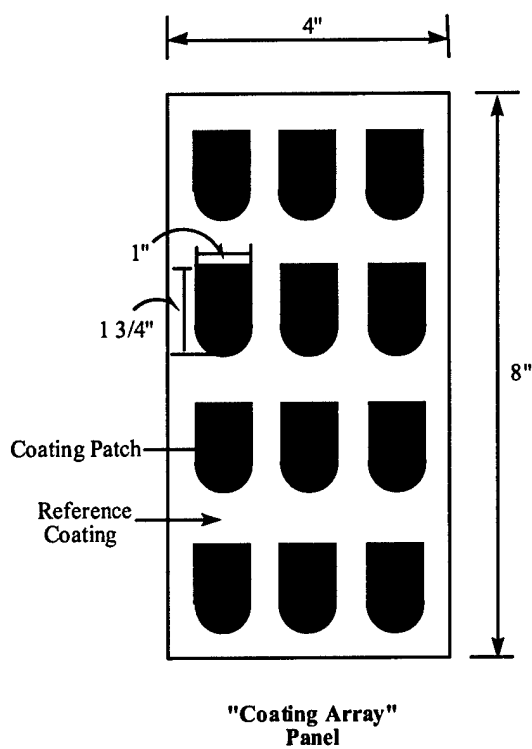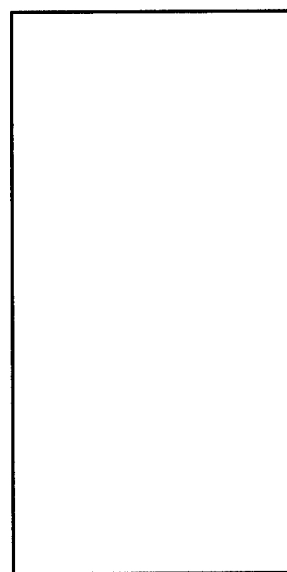
Figure 4
Configurations of NDSU Coating Formats on 4" x 8" panels

Summary of Preliminary Barnacle Settlement Results: There was a large variability in the settlement of barnacles among the replicates of any particular coating type. This made it statistically difficult to make any distinctions among the various coating types submitted regarding their relative anti-fouling capability. Barnacle settlement on the coating patch arrays of Coating I were statistically similar to that of 4"x 8" panels completely coated with Coating I.

University of Birmingham (Preliminary Enteromorpha Spore Settlement Testing)

It must be noted at the outset of this section that results obtained thus far from this laboratory are *preliminary* and must be interpreted as such. There were several issues that arose regarding possible NDSU sample incompatibility with University of Birmingham testing protocols, which limit the interpretation of the data presented below. These issues are in the process of being resolved. The data below is included here in order to show early *trends* rather than quantitative results.

Assay Methods: Standard leaching and settlement methods were used. The water channel was used to determine strength of attachment of sporelings.

Leaching: The slides were leached for 24 h in stirred distilled water.

Settlement of Enteromorpha zoospores: Zoospores were obtained from mature *Enteromorpha* plants by the standard method. Zoospores were settled on slides in individual quadriperm dishes containing 10 mL of zoospore suspension (1.5×10^6 spores ml^{-1}) in the dark at ~20°C. After 1 h the slides were gently washed in seawater to remove zoospores that had not attached. The samples were fixed in 2 % glutaraldehyde in seawater, washed in sea water followed by distilled water and allowed to air dry.

The density of zoospores attached to the surface was counted on each of 3 replicate slides using an image analysis system attached to a fluorescent microscope. Spores were visualised by autofluorescence of chlorophyll (but see comment in results section). Counts were made for 30 fields of view (each 0.17 mm^2) on each slide.

Spore viability test: Spore motility was used to indicate whether any compounds that affected spore viability were leaching out of the coatings. At the washing stage (1h post addition of spores), the seawater containing unsettled spores was poured into 20 ml glass vials and placed in unilateral light (by a window). If any inhibitory compounds leach out of the coatings, the swimming spores loose their ability to swim (spores are negatively phototactic and quickly move to the shaded side of a container) and hence remain in suspension.

Growth of sporelings: Sporelings were cultured in enriched seawater medium in individual compartments of a quadriperm polystyrene dish under illuminated conditions. The medium (10 ml) was refreshed every 2 days and the sporelings cultured for 8 days.

Two spore settlement densities were used viz 1.5×10^6 and 3×10^6 spore ml^{-1}.

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Biomass was estimated at 8 days by extraction of chlorophyll a and data are expressed as weight of chlorophyll a / unit area of test surface. The sporelings were removed from half of each slide and biomass estimated by extraction of chlorophyll a. The biofilm on the other half of each slide was left intact for determination of the strength of attachment in the flow channel. Chlorophyll a was extracted in DMSO and the concentration was determined spectrophotometrically using the equations of Jeffrey and Humphrey, 1975.

Strength of attachment of sporelings: The remaining sporelings on the slides settled at the higher density were exposed to a wall shear stress of 53 Pa in the water channel. The biomass remaining was again carefully removed and the chlorophyll a content determined as above.

Typical images of the settlement of *Enteromorpha* zoospores on the coatings after 1 h settlement are given in Figure 6. The spores on glass and the reference (X) coating look normal. The spores on the other coatings are distorted and those on coatings II and III had started to disintegrate and bleach. Note also the deterioration in quality of 48. This deterioration is probably due to the presence of the PEG moiety in this coating.
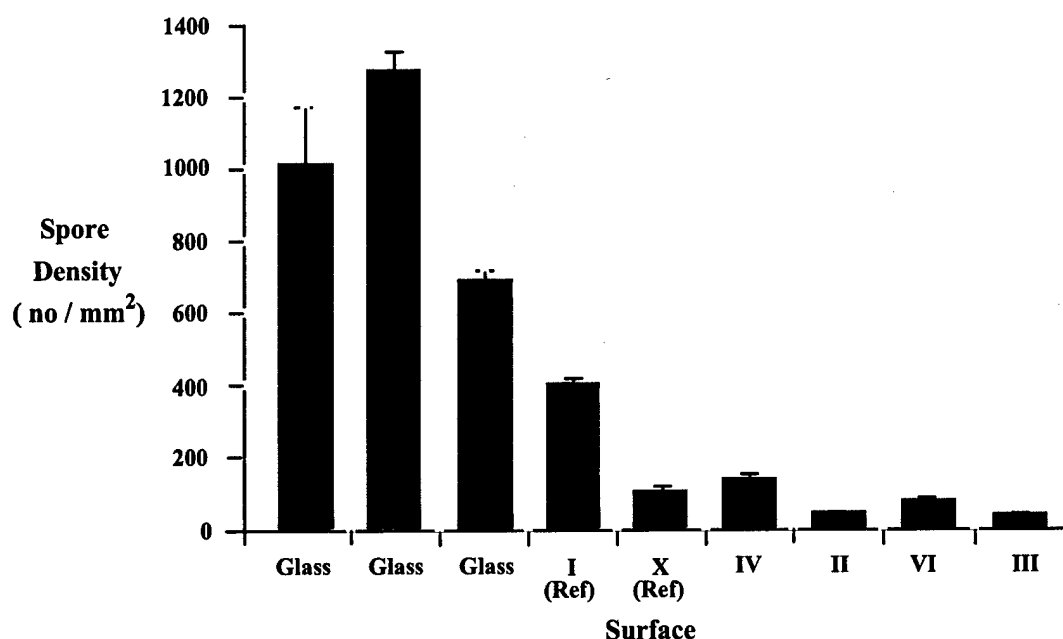
Figure 4.
Enteromorpha Spore Settlement on Coated Microscope Slides (purple designates
a separate assay)
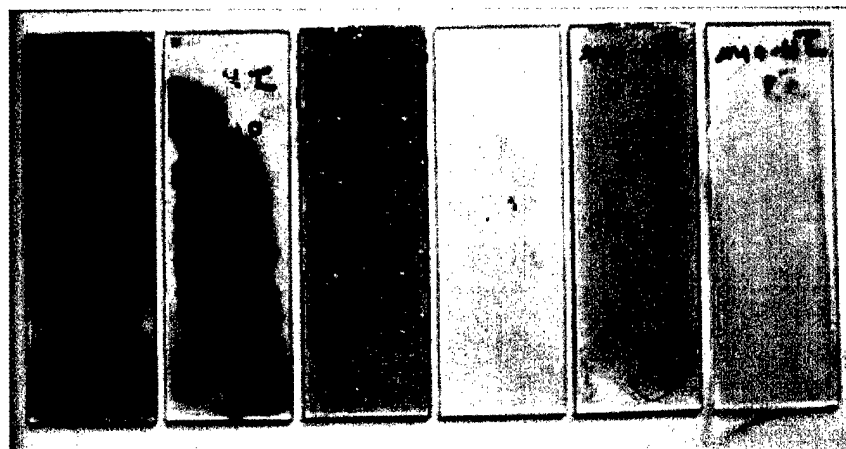
Figure 5.
Typical images of slides after 8 day immersion and growth of sporelings. From left: Glass, Ref Coating X, Coating IV, Coating II, Coating VI, and Coating III. Note the rough surface on sample Coating IV.
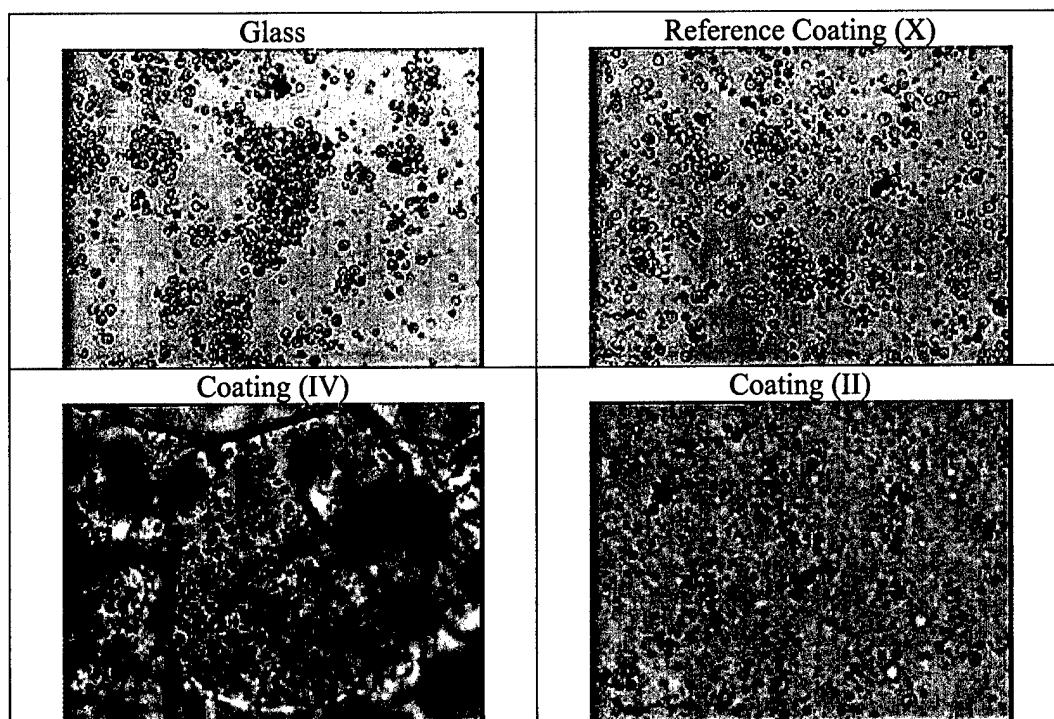
Figure 6.
Typical images of the settlement of *Enteromorpha* zoospores on the coatings after 1 h settlement
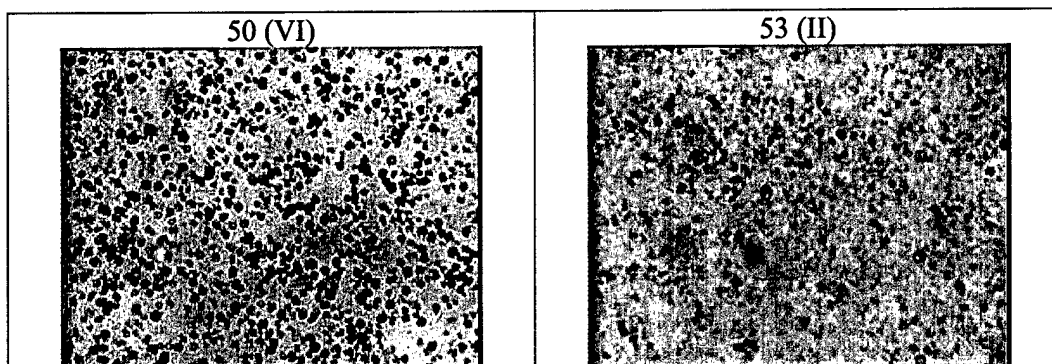
Figure 6 (continued).
Typical images of the settlement of *Enteromorpha* zoospores on the coatings after 1 h settlement
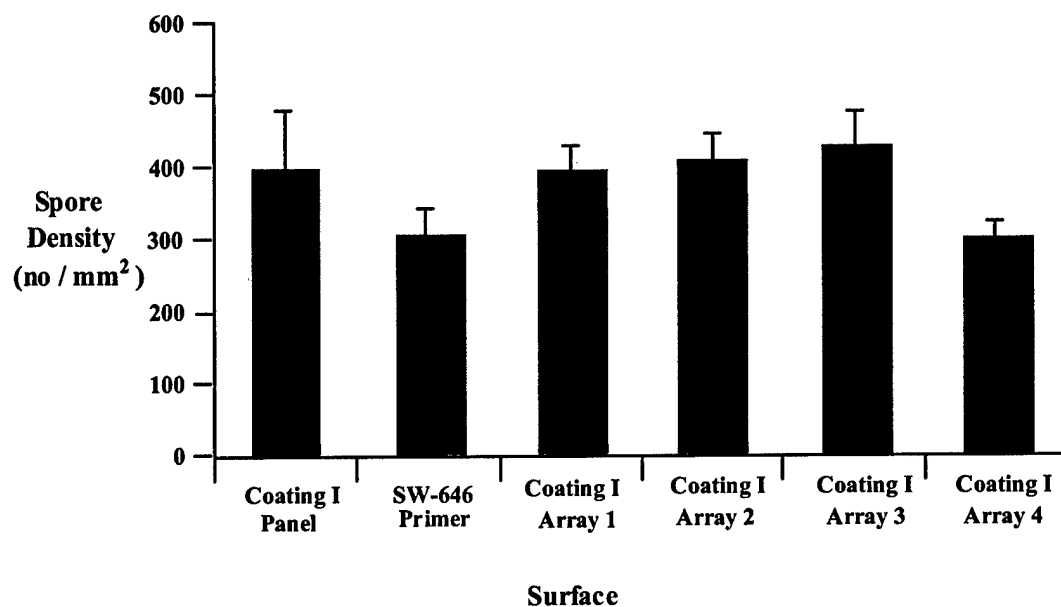
Figure 7
Comparison of *Enteromorpha* Settlement on Fully Coated Panels with Settlement on Coating Patch Arrays

Summary of Preliminary Enteromorpha Spore Settlement Testing: All of the NDSU coatings (except reference coating TR-1) showed severely impeded spore settlement during the 1 hr assay (Figure 4). Coatings containing the Triclosan biocide showed little settlement throughout the 8 day settlement (Figure 5). Most of the spores which settled on Triclosan containing surfaces were damaged or dead (Figure 6).

University of Hawaii (Preliminary Tube Worm Settlement Testing)

Coatings (I, II, III, IV, VI, and X, Table 1) were applied to 1" x 3" microscope slides and subjected to the Hawaii Tube Worm settlement assay, followed by foul-release measurements via a flow cell apparatus.

Summary of Preliminary Tube Worm Settlement Testing: "Conclusion: Treatments II and VI had significantly better antifouling properties than the reference coating (X). Coating II is the best performer I've seen all year. It exhibited antifouling properties and exceeded our criteria for a foul release coating that deserves more detailed testing."…..Chris Bird, University of Hawaii (Smith Laboratory)

Summary of Achievements
- Chemical incorporation biocidal, hydrophilic, and cross-linking moieties onto a single silicone backbone.
- Demonstration of coating film formation using new biocide-containing silicone resins.
- Promising results from various test sites on NDSU's first iteration coatings.

Future work
- Continuing the design, synthesis, and characterization of novel silicone resins.
- Enhancing coating performance through formulation
- Quantitative measurement of biocide leaching rates from coatings via HPLC.
- Transition resin / coating synthesis and characterization to combinatorial high-throughput tools and systems.

3.2 Self-Stratifying Siloxane Polyurethane Coatings

Personnel: Dean Webster (Professor of Polymers and Coatings), Abdullah Ekin (Graduate Research Assistant), Partha Majumdar (Graduate Research Assistant), Jim Bahr (Research Engineer), David Christianson (Research Specialist).

Initial Synthesis Experiments

Work has just gotten underway for the synthesis of libraries of siloxane-urethane coating systems. Much of the effort thus far has involved the development of some initial formulations that can be used as a starting point for the preparation of additional combinatorial libraries.

First, we identified all of the variables that could impact the performance of a crosslinked siloxane-urethane coating. These are listed in Table 3.

Table 3. Key Variables to be explored in the design of self-stratifying coatings

Poly(dimethylsiloxane) molecular weight
Poly(dimethylsiloxane) end groups (hydroxyl or amine)
Poly(caprolactone) end-capping of PDMS
Isocyanate Crosslinker Type and Functionality
Other Polyol Type (acrylic, polyester, polyether, polycarbonate)
Other polyol equivalent weight
Low MW polyol
Ratio of polyols
Level of PDMS
Isocyanate to polyol ratio
Catalyst
Pot life extender
Other solvents

As a starting point, we selected Tone 0305 polycaprolactone polyol from Dow as the main polyol and then a trimer of IPDI (isophorone diisocyanate) as the polyisocyanate.

We also prepared lab batches of two hydroxy functional PDMS oligomers at 10,000 and 50,000 g/mol (theoretical). Bis(hydroxypropyl)tetramethyl disiloxane and D4 were purchased. The final molecular weight is controlled by the ratio of disiloxane and D4 (see Scheme 1). Polymerization temperature was 80°C and tetrabutyl ammonium hydroxide was used as the catalyst. Characterization of these polymers will be done when the new columns are installed on the GPC.
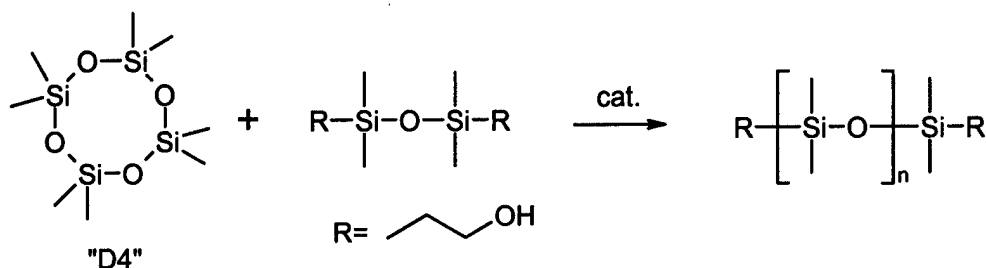
Scheme 1. Synthesis scheme for functional PDMS oligomers.

In synthesizing these reactive polyurethane coatings in the combinatorial equipment, we need to make sure that the coating formulations have sufficient "pot life" to remain ungelled and low viscosity until after the coatings are applied. Once all of the components are mixed, the reactions start taking place. If the formulations are too reactive, they may gel in the vials before they can be applied. Or, the viscosity may become too high to be applied successfully.

Fortunately, for polyurethane systems it has been found that 2,4-pentanedione (2,4-PD) functions as an effective pot life extender. It can inhibit the reaction in the container, but after the film is cast will evaporate and allow the reaction to proceed. Usually, in commercial coatings the pot-life extender level is carefully optimized to yield just the right balance of pot life and coating drying time. However, for our experiments we would like to overdo the level of 2,4-PD to provide extra insurance that the coatings do not gel prematurely. Since we are focused on coating performance, we will be force drying these coatings at 80°C. Thus, we expect that we can drive off the 2,4-PD in the curing process.

As a check, two formulations were prepared; one contained 10% 2,4-PD and the other had no 2,4-PD. These were both force dried under the same conditions and the T_g checked to determine if the properties of the coating were affected by the presence of the 2,4-PD. (Note, the only thing in these coatings that would affect the T_g would be the level of crosslinking since the compositions were the same.) The T_gs of the two coatings only differed by 1.5 degrees, with the 2,4-PD coating having the higher T_g. Thus, we were assured that using an excessive amount of the pot life extender would prevent premature gelation without seriously affecting the properties of the coatings.

Combinatorial Pot Life Study

Very often the combination of catalyst and pot life extender has to be carefully optimized to balance stability and cure rate. To obtain a quantitative measure of the pot life, it is common practice to measure the viscosity of the coating formulation as a function of time after the crosslinker is mixed with the polyol. The time for the viscosity to double is commonly used as an indication of the pot life. Since we have an automated system to mix coating formulations and measure viscosity, why not use the combinatorial coating formulation system to conduct a pot life study?

To use the system to conduct this study requires that the sequence of events be reprogrammed. To determine the feasibility of this approach we operated the sequence of events semi-manually.

For this preliminary study, we decided to look at four different catalysts, with one at two different levels for a total of five formulations. The isocyanate crosslinker was added last, and the viscosity measured at regular intervals until it had doubled. Then the experiment was repeated with the next sample. A graph of the viscosity data as a function of time is given in Figure 8.
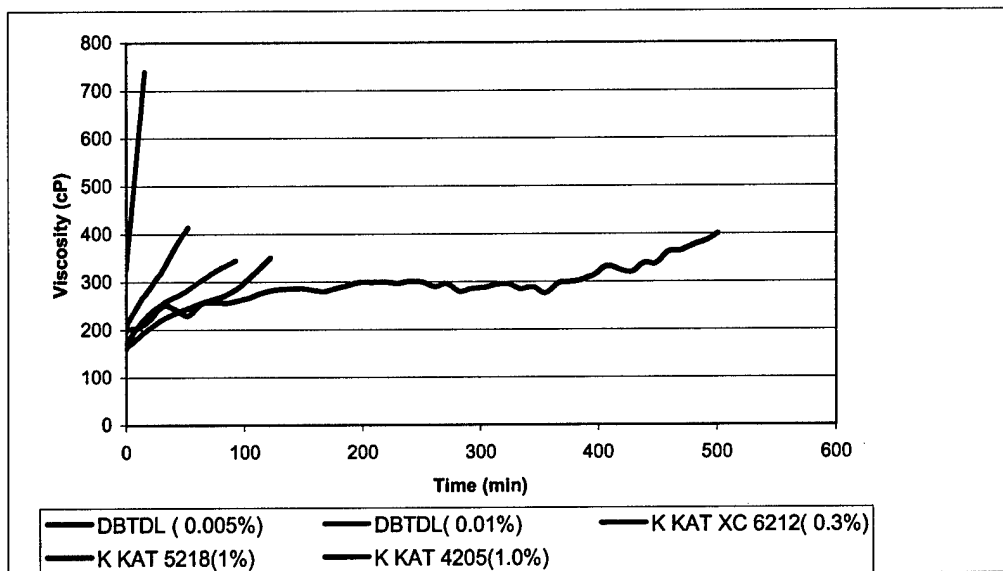
Figure 8. Viscosity versus time for combi pot life study. All formulations contained 5% 2,4-pentanedione.

From the graph, it is clear that the K-Kat 5218 has the longest pot life. However, we found that this coating also would not cure even after doubling the time in the oven. This experiment is a good illustration of the fact that focusing on just one property in a screening measurement can often be misleading. In this case it is important to have a good pot life *and* have a coating formulation that cures under the required conditions.

Some significant reprogramming of the system is required in order to conduct an efficient pot life study such as this in a full 4 x 6 array. Issues such as viscosity measurement frequency, sequential or parallel operation need to be resolved. However, being able to conduct this kind of study will be extremely beneficial in catalyst development and also for optimizing coating formulations.

Combinatorial Siloxane-Urethane Coatings

The combinatorial approach lends itself to full-factorial experiments to explore the impact of key variables on performance. Now that we have quite a bit of preliminary work accomplished, we have initiated the combi experiments necessary for identifying key variables as well as compositions with unique performance properties.

Our first significant experiment involved the preparation of a library of 24 siloxane-urethane coating samples. Variables were six levels of hydroxy terminated PDMS (10,000 g/mol) from 5 percent to 30 weight percent, and four levels of added toluene solvent. We speculated that solvent content could play a role in the organization of the coatings into the separated siloxane and urethane layers. As discussed above, the remaining components are: Tone 0305 polycaprolactone polyol, IPDI trimer, dibutyl tin dilaurate catalyst, and 2,4-pentanedione pot life extender.

The coatings were prepared and the contact angles measured in the surface energy system. We ran into a problem with the flow out of the coatings, so only were able to measure water contact angles of the coating array. This data is presented in Figure 9.
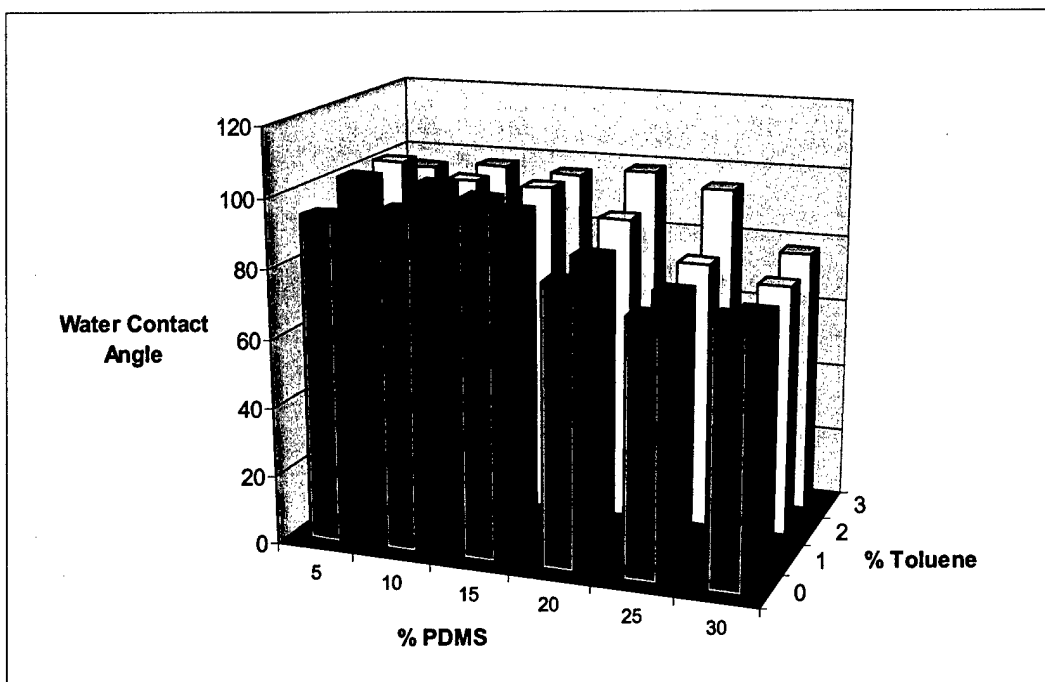
Figure 9. Water contact angle of the siloxane-urethane coating array.

While this data is highly preliminary, the trends are intriguing. First is that the contact angle generally decreases with increasing siloxane content. This may indicate some phase mixing taking place between the siloxane and the polyurethane. There also appears to be an effect of the solvent content. Note that the 3% toluene contact angles are higher at higher levels of siloxane than the coatings that contained lower levels of toluene. Solvent content may be playing a role in the organization of the surface after coating application as the solvent evaporates.

Our next step is to repeat this experiment and resolve the coating application issues that prevented the full determination of surface energy. We are also planning on rerunning the surface energy measurements after conditioning the coating array in artificial sea water to see how stable these surfaces are.

We are also in the process of synthesizing several libraries of both hydroxyl and amine terminated siloxane oligomers, as well as caprolactone end-capped siloxane polymers. Preliminary laboratory work has been completed and our first library of hydroxy terminated siloxane polymers was prepared and is being characterized.

Other future work will include some transmission electron microscopy to obtain evidence for the stratification and thermal and mechanical analysis of the coatings to determine if phase mixing is occurring between the siloxane and urethane phases. Our plan also includes preparing and storing multiple sets of coating libraries for testing with the pull off adhesion system when it is available early next year.

3.3 Establishment of the Combinatorial and High Throughput Laboratory

Personnel: Dean Webster (Professor of Polymers and Coatings), James Bahr (Research Engineer), David Christianson (Research Specialist), Karen White (Manager of Engineering Operations), and John Simon (Facilities Analyst and Cleanroom Manager). Abdullah Ekin and Partha Majumdar (Graduate Research Assistants). Joni Altringer (Microbiology), Christy Gallagher-Lein (Chemistry and Mechanical Engineering), and Jason Greenwood (Mechanical Engineering), Undergraduate Research Assistants.

Facility Modification

The NDSU Combinatorial and High Throughput Laboratory will eventually be housed in the new Research II facility currently under construction. In the interim, space was identified in Dunbar Hall that would be suitable for the equipment. Dunbar Room 56 was equipped with three laboratory benches and two fume hoods. To make it suitable for the Symyx equipment, several modifications were made. One of the benches was removed to provide room for the triple glove box that houses the Synthesis System. The remaining two benches were resurfaced. In addition, the walls were repainted, and the floors and hoods cleaned. Ethernet and appropriate electrical wiring was installed for each Symyx system. Elephant trunk ventilation was also provided for the glove box and other systems. A layout of the laboratory is shown in Figure 10.

Figure 10. Layout of Combinatorial and High Throughput Laboratory
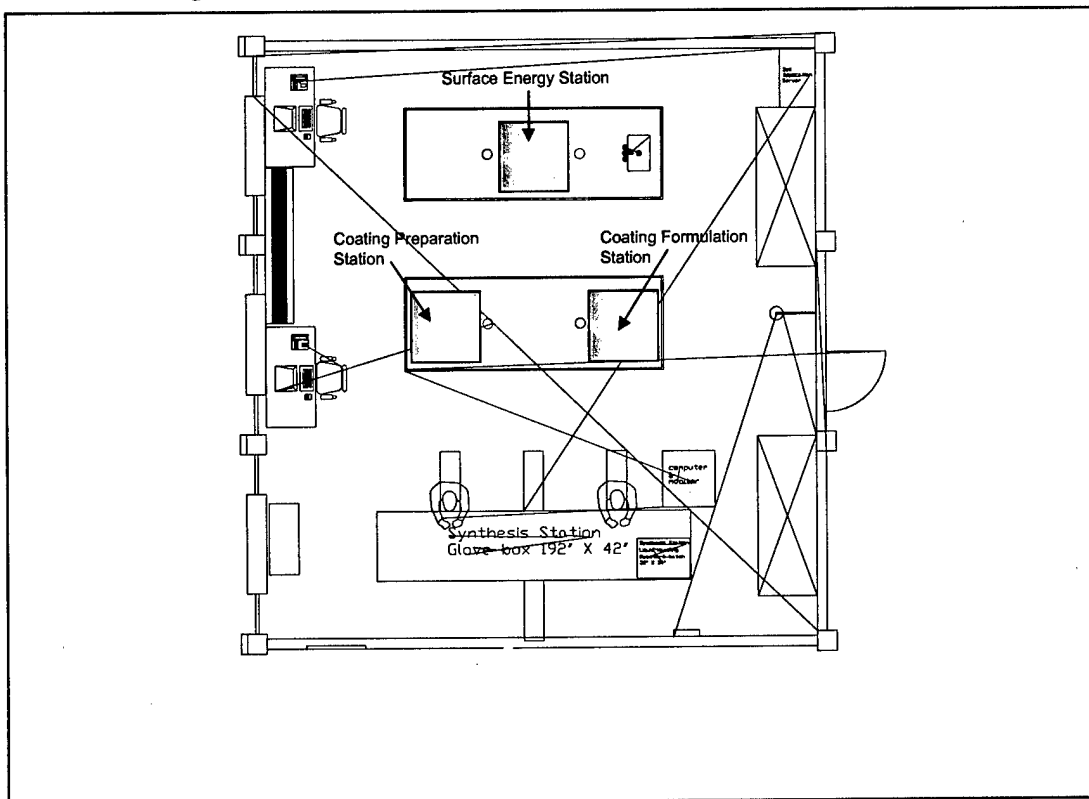
Combinatorial Workflow for Coating Development

Coating formulation requires a large number of steps and activities. Breaking the process down into its individual steps and then determining which steps are critical and require automation generates the coating workflow. The big picture view of the coating workflow is shown in Figure 11. This involves the steps of experimental design, polymer synthesis, polymer analysis, coating formulation, coating formation, and coating analysis.

For this initial phase of funding, we identified the minimal components of the workflow required to close the loop on the combinatorial process. These components are a simple batch polymer synthesis system, a coating formulation system including viscosity measurement, a coating application (film formation) system to apply the coatings to a substrate, and our first piece of analysis equipment, the coating surface energy measuring system. This is all tied together with a robust suite of software tools for library design, experiment execution, data storage, and data mining.
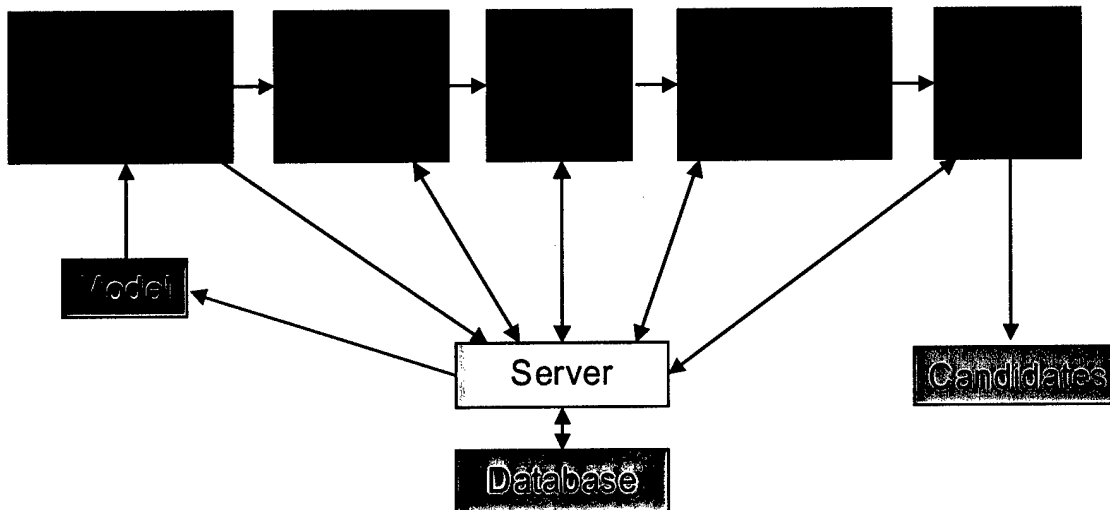
Figure 11. Workflow for combinatorial and high throughput coating development.

From this initial system we can add components to enhance our capabilities and fill in the gaps in the overall workflow.

Installation of Combinatorial Equipment

In Phase I, we installed four pieces of equipment supplied by Symyx Discovery Tools. These were Synthesis System, Coating Formulation System, Coating Application System, and Coating Surface Energy System. For each system installed, a set of Factory Engineering Tests were developed by Symyx and agreed upon by NDSU. These tests verified key operational parameters for each system and were used to verify acceptable performance.

Prior to shipping of the system, one or more NSDU employees traveled to Symyx for training on the software and the operation of the system to be delivered. This visit also included testing of the system to ensure compliance with the Factory Engineering Test standards. Once the system was approved, it was crated and shipped to NDSU. Symyx personnel then traveled to NDSU to uncrate and install the system and again ensure that it met the Factory Engineering Test parameters. Additional training was also provided by Symyx during the on-site visits.

Synthesis System

The synthesis system was delivered on September 27, 2002 and is composed of a reaction system that is housed in a triple glove box to provide an oxygen and moisture free environment. A photo of the glove box in the laboratory is in Figure 12.
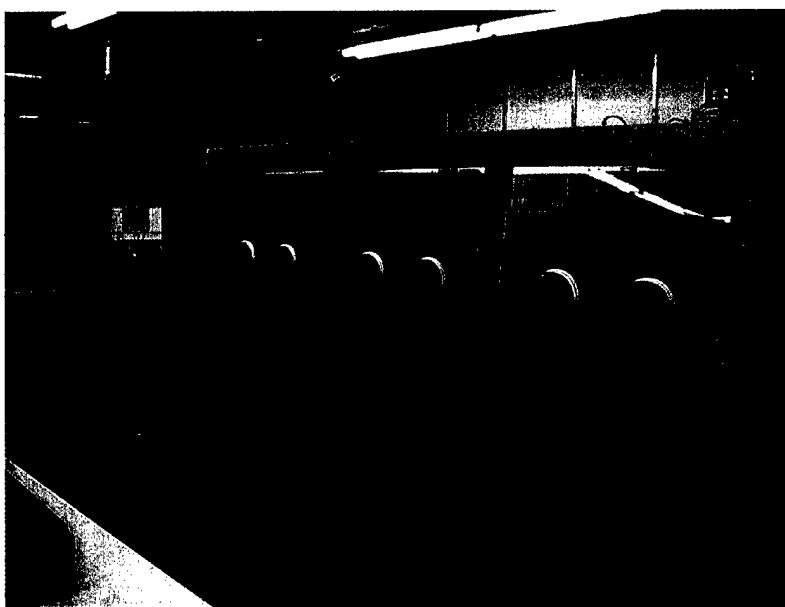
Figure 12. Triple glove box housing the synthesis system.
Note: This equipment may be used in a polymer and coating work flow developed by NDSU working with Symyx and covered by U.S. Patent No.'s 6,004,617 and 6,346,290 to Schultz et al., Symyx Technologies, Inc.

The reaction system consists of a platform with an array of nine wells for receiving standard size blocks of reaction vessels. The center three sections are heated and magnetically stirred. Two liquid handling robot arms are used to transfer stock solutions into the individual reactor vessels. Each liquid handling robot has two syringes, 5.0 ml and 500 µl, for delivering low viscosity reagents. Reactor arrays ranging in volume from 1 ml (96 reactors) to 20 ml (6 reactors) are supplied with the system. Larger sized containers are usually used for holding stock solutions and monomers while the 6 x 4 and 8 x 12 arrays are used for synthesis of polymers and oligomers. A photo of some of the vessel sizes available is in Figure 13.

The glove box system is used to maintain an oxygen and moisture free environment for the reagents used in the reactions. Unlike using a simple round-bottom flask, the individual reactors cannot be purged with nitrogen and the reagents are handled in the open during transfer

operations. Thus the entire environment has to be an inert atmosphere. The glove box also has a built in freezer/refrigerator for storage of raw materials.
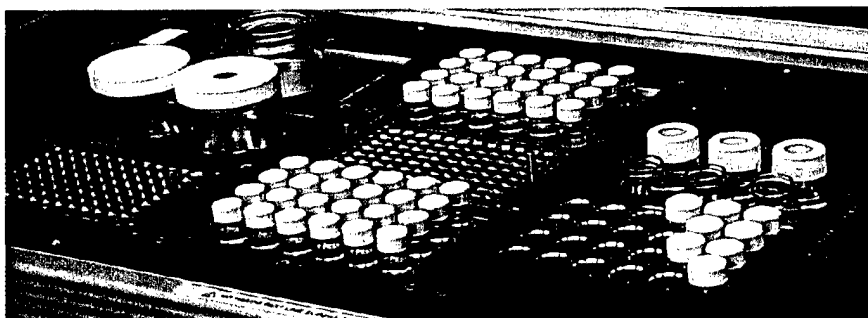
Figure 13. Various sample array configurations for the synthesis system.
Note: This equipment may be used in a polymer and coating work flow developed by NDSU working with Symyx and covered by U.S. Patent No.'s 6,004,617 and 6,346,290 to Schultz et al., Symyx Technologies, Inc.

Initial Synthesis Experiments

To help understand some of the operating parameters and gain experience in operating the synthesis system, several free radical solution polymerizations were run.

In the first experiment, it was important to determine if there was any uneven heating across the reactor block as well as begin to become familiar with the extent of variation from sample to sample that we might expect. Thus, we conducted a very simple free radical solution polymerization of three monomers (styrene, butyl acrylate, hydroxyethyl acrylate), using Vazo 67 (azobisisovaleronitrile) as initiator and toluene as the solvent. The experiment consisted of 24 identical polymerizations and the polymerization was run for 4 hours at 80°C. Since initiation rate of thermal initiators is very sensitive to temperature variation, the results from this experiment might alert us to any substantial variations in temperature from reactor well to reactor well in the array. Variations in dispensing of monomer and initiator will also be reflected in this experiment.

Gel permeation chromatography was run on each polymer synthesized. The results are shown in Table 4. At the bottom of the table, the average and standard deviation are listed for number average molecular weight, weight average molecular weight and the polydispersity. All of these values are low and appear to indicate that there is very little well-to-well variation in the system.

Table 4. GPC results for free radical polymerization experiment.

Sample	Mn	Mw	PD
A1	22828	45207	1.98
A2	22792	44505	1.95
A3	23299	45818	1.97
A4	24126	46393	1.92
A5	23969	47239	1.97
A6	24717	47053	1.90
B1	25050	47151	1.88
B2	24520	46222	1.89
B3	24290	45100	1.86
B4	24386	45854	1.88
B5	24812	46544	1.88
B6	25711	47675	1.85
C1	25696	48143	1.87
C2	25482	47187	1.85
C3	23911	45612	1.91
C4	24835	45602	1.84
C5	25004	45508	1.82
C6	24779	45602	1.84
D1	24957	46315	1.86
D2	24761	45945	1.86
D3	25211	45391	1.80
D4	24655	45238	1.83
D5	23976	45063	1.88
D6	24747	45963	1.86
Average	**24521**	**46097**	**1.88**
Std. Dev.	**776**	**919**	**0.05**
% Std Dev	**3.17**	**1.99**	**2.56**

After we obtained these results we realized that we did not know the variation in the GPC measurement itself. One sample was selected and GPC measurements were run 10 times. This data is listed in Table 5. Note that the standard deviation for the repeated runs is higher than what was obtained for our reactor array. Comparing the two sets of data using a t-test indicates that there is no statistical difference between the two sets of data.

Table 5. GPC results for repeated runs.

Run	Mn	Mw	PD
1	21533	44026	2.04
2	21707	44456	2.05
3	22881	44981	1.97
4	22745	45152	1.99
5	23433	45946	1.96
6	23317	46281	1.98
7	25998	46851	1.80
8	26016	47107	1.81
9	26026	47417	1.82
10	25696	48143	1.87
Average	23935	46036	1.93
Std. Dev.	1824	1360	0.09
% Std Dev.	7.62	2.96	4.91

As before, we used GPC to characterize the molecular weight. Solvent was removed from the polymer solutions and differential scanning calorimetry (DSC) used to measure the polymer T_g. The data was then used by Design-Expert to develop models that fit the data and are statistically significant. A response surface map for number average molecular weight is shown in Figure 14. The best fit to the data was a cubic equation, which results in the curvature shown. These results are confounded, however, by the fact that different compositions will have different hydrodynamic volume in solution, thus have different apparent molecular weight in the GPC experiment. It also must be pointed out that the inhibitor was not removed from the monomers in this experiment. Since different inhibitors are used for the different monomers, this molecular weight variation could be a result of the inhibitor type and concentration in each composition. However, manufacturers of acrylic polymers for coatings usually do not remove the inhibitors before conducting free radical polymerizations. So, this suggests additional experiments to explore the effect of inhibitors on molecular weight of copolymers.

We modeled the T_g data using the Fox relationship and the response surface is shown in Figure 15. (Note that the surface is a plot of $1/T_g$, so the graph goes up when the T_g goes down.) The coefficients of the fit represent the T_gs of the respective homopolymers. These values are: styrene, 66.2°C; butyl acrylate, -36.8°C; hydroxyethyl acrylate, -35.9°C. The discrepancy between these values and the literature values (100, -54, -15, respectively) are probably a result of the low molecular weight of these polymers. However, note that in one single experiment, the T_g values of three different homopolymers were determined for the molecular weight range studied. A series of experiments like this could generate models for the T_g contribution of a wide variety of monomers as a function of polymer molecular weight.

This kind of comprehensive data does not exist anywhere in the literature and would be valuable for those involved in designing copolymer systems. Large sets of combinatorial experiments could be conducted and used to build empirical models that could predict the effect of composition, initiator type, temperature, etc. on fundamental properties.

DESIGN-EXPERT Plot

Mn
X1 = A : Styrene
X2 = B : Butyl Acrylate
X3 = C : Hydroxyethyl acrylate
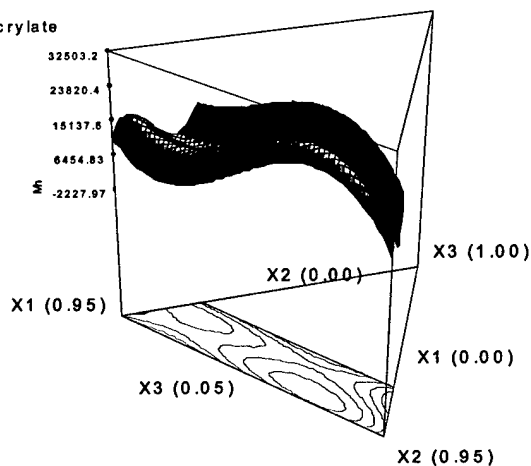
Figure 14. Response surface for M_n.

DESIGN-EXPERT Plot

1.0/(Tg + 273.00)
X1 = A : Styrene
X2 = B : Butyl Acrylate
X3 = C : Hydroxyethyl acrylate
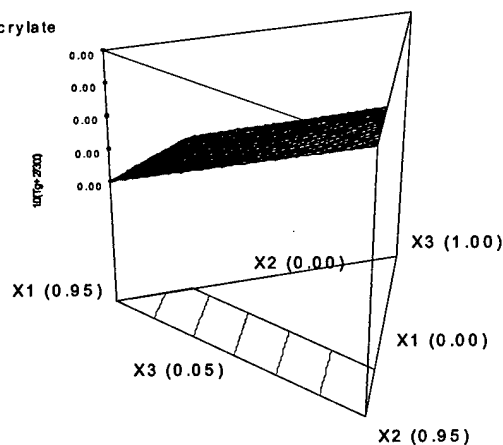
Figure 15. Response surface for 1/Tg.

Due to the interesting data obtained from this experiment, it was repeated, however, the inhibitors were removed from the monomers. In addition to the molecular weight analysis by GPC, determination of the T_g using DSC, the viscosity of the resin solutions was determined using the viscometer on the formulation system (see next section), and the conversion was also determined. This time the model fit of the molecular weight data did not exhibit any curvature, however, a trend in molecular weight as a function of composition was again observed (Figure 16). Whether this trend is due to variation in the hydrodynamic volume of the polymers or to a

real effect based on copolymerization kinetics is not known. A more absolute method for determining polymer molecular weight such as MALDI-TOF (matrix assisted laser desorption ionization mass spectrometry) would provide that data unambiguously.

Figure 16. Response surface for Mn.

The response for T_g is qualitatively similar to that of the previous experiment, however, a cubic model is reported by Design-Expert to be a better fit than a linear model.

The response surface for viscosity is shown in Figure 17. Note that there is an optimum low viscosity in the model of this response. This response is significant since finding an optimum low viscosity is beneficial for anyone developing low VOC (volatile organic content) coating systems.

These experiments demonstrate the power of the combinatorial approach. These sets of data were generated in a single synthesis experiment of 24 polymers. To make 24 polymers in a standard laboratory setting would require several weeks worth of effort. Even including the pre-combi preparation (monomer purification, solvent degassing, experimental design) and post-combi activities (sample work up, GPC and DSC analysis), a significant amount of useful data has been generated in a very short period of time.

DESIGN-EXPERT Plot

Viscosity
X1 = A : Styrene
X2 = B : Butyl Acrylate
X3 = C : Hydroxyethyl acrylate
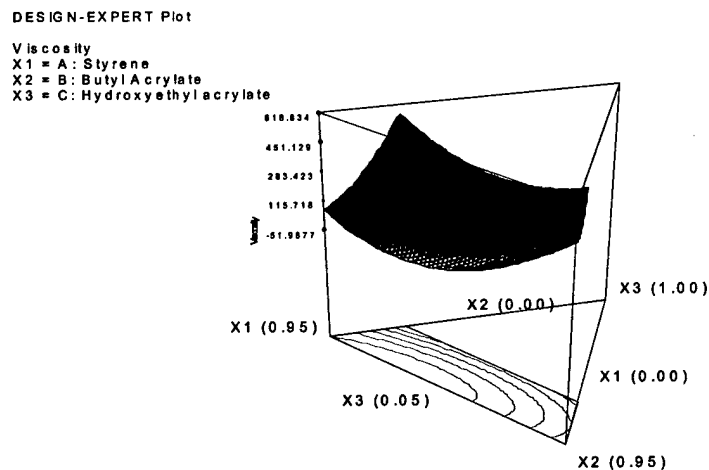
Figure 17. Response surface for viscosity.

Coating Formulation System

The coating formulation system was installed in January 2003. (This was the coldest week of the year!) The system consists of a two-arm robot with a platform very similar to that of the synthesis unit (see Figure 18). Thus, there are nine wells for holding array blocks, with the three center wells having heating and magnetic stirring. Since this system will be used to dispense higher viscosity liquids than the synthesis system, the left robot arm is fitted with a pipette with disposable tips. Using disposable tips minimizes the possibility of cross contamination of the reagents and eliminates the need for cleaning of the tip between reagents, speeding up the dispensing process.

This system is optimized for preparing 6 x 4 arrays of coating formulations. This size vial provides 3-6 ml of solution to use for preparation of multiple sets of coatings in a variety of formats.
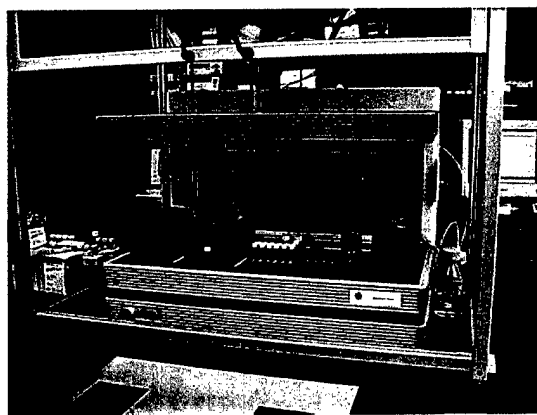
Figure 18. Coating Formulation System

The second (right) robot arm holds a unique custom-designed viscometer that is used to measure the viscosity of the coating formulations (Figure 19). The viscometer tips are interchangeable, that is, a new measuring tip is used to measure the viscosity in each coating formulation. A tip rack holds 24 tips in a 6 x 4 arrangement. The viscometer is calibrated using viscosity standards. After a tip is used, it is ejected into a beaker containing solvent. Then the tips are cleaned and returned to use.

The system is programmed with a software routine to reduce the viscosity of the coating array to a target value. This process involves repeated additions of solvent, mixing, and viscosity measurement. This gives us the option of preparing libraries of coatings that have either the same volume solids or the same viscosity.
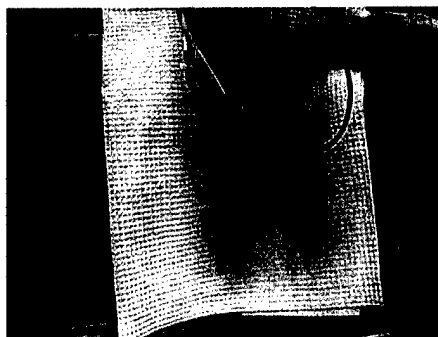
Figure 19. Close up photo of the rapid viscometer.

Coating Film Formation System

The coating preparation system was also installed in January 2003. A two arm robot is mounted on a flat base. The base is used to mount the pipette racks, coating sample array, coating substrates, and the ultrasonic bath and air knife. The right robot arm is used to deposit the coating formulation in a bead on the substrate to be coated. The left robot arm holds a doctor blade that is used to spread the bead into a coating. When the doctor blade is finished, it then is given a solvent wash in a three-chambered ultrasonic bath, and then dried with an air knife (Figure 20).
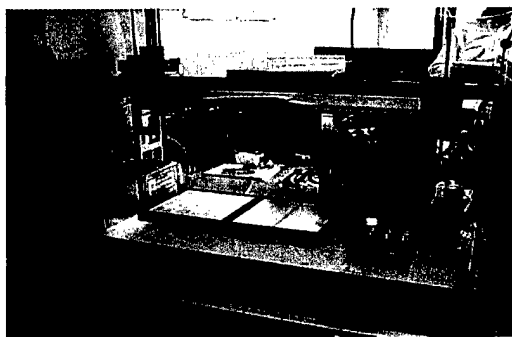
Figure 20. Coating Film Formation System.

The coating substrate holders were designed to hold standard 4" x 8" coating substrates, which are available from several suppliers. Two 4" x 8" substrates are required for a complete library of 24 elements. There are also two vacuum holders so that the library can be duplicated on two sets of substrate at one time. Steel and aluminum panels come in this standard size. Glass and plastic substrates can also be used depending on the requirement of the experiment (Figure 21).

Figure 21. Close-up of doctor blade and substrate holder.

The feet on the side of the doctor blade can also be adjusted to provide a range of wet film thicknesses. The drawdown approach is also more flexible and forgiving than a spray or spin coating approach. Since drawdowns are used extensively in the coatings industry for initial development work, it is also easier for a typical coatings scientist to relate to this method of coating.

Another benefit we have found in the way this system is designed is that relatively "large" areas of coating are produced, compared to other efforts reported in the literature. We believe that this approach has several distinct advantages. The area of the coating spots is large enough that off-the-shelf equipment for measuring gloss, color, or film thickness can be used. Using the standard substrates means that we can use these test panels in standard test equipment, such as accelerated weathering or corrosion testing (of course, bare areas between the coatings have to be protected). We are also testing to determine if these test panels can be used directly for immersion testing for the characterization of initial fouling settlement on the coatings.

Initial Experiments

A number of initial experiments have been carried out to gain experience in the operation of the equipment as well as understand the reproducibility of the experiments.

Viscosity Measurement. The viscometer on the coating formulation system is calibrated over a wide range using Newtonian viscosity standards. Operational parameters have been fixed to a

Table 6. Viscosity measurements of Polymac resin diluted with MAK.

Sample	Brookfield	Combi Visc (cP)					
% Solvent	(cP)@100 rpm	1	2	3	Average	Std. Dev.	% Std.Dev.
30.0	51	67.7	58.9	75.9	67.5	8.49	12.58
20.0	250	289.1	294.0	308.1	297.1	9.85	3.32
17.5	314	396.9	406.3	406.3	403.1	5.40	1.34
15.0	435	563.1	583.2	558.4	568.2	13.19	2.32
12.5	928	1079.1	1067.9	1054.6	1067.2	12.26	1.15
10.0	1510	4338.8	3632.0	3978.6	3983.1	353.42	8.87

single angular displacement of the viscometer paddle and displacement frequency. To gain an initial understanding of the relationship between the automated viscometer and a standard Brookfield viscometer, a series of samples were prepared using Polymac 57-5776 (supplied by Eastman), diluted with methyl amyl ketone solvent in the laboratory. The same series of dilutions was prepared using the coating formulation system and each dilution was prepared three times. Brookfield viscosity was measured on the laboratory samples and the viscosity was measured using the combi unit. The data is listed in Table 6.

The combi viscosity measurement is highly reproducible in the middle ranges of viscosity (200-1000 cP). The variation increases for both the high and low viscosity samples tested. It must be kept in mind, too that this experiment also reflects variations in dispensing and mixing the materials. While the Brookfield values and the combi values are not an exact match, they do correlate with each other (Figure 22). Since this resin is possibly non-Newtonian, some of the differences in the measurements could be a reflection of the effective shear rates of the two different methods. What is important for screening purposes is that the viscosities be in the proper order.

We are planning more extensive experiments to fully characterize the effect of the viscometer operational parameters on the values obtained using well-characterized non-Newtonian resin solutions.

Formulation System. Pre-dilution is required to lower the viscosity of the resin and also improve the accuracy of the catalyst and additive dispensing.
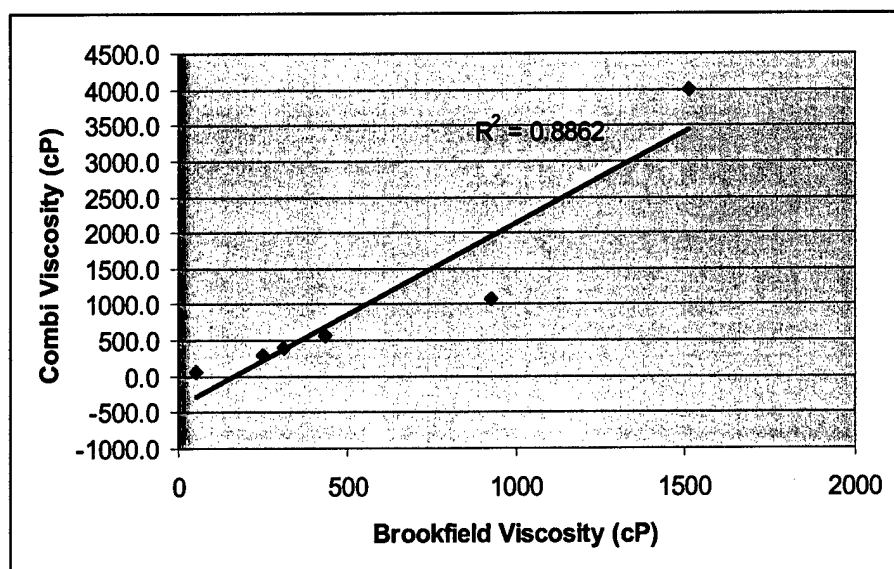
Figure 22. Correlation plot of Brookfield and Combi Viscosity.

To attempt to provide some variation in coating properties, we prepared six formulations, listed in Table 7. The formulations were prepared in the laboratory using standard practices, and then each formulation was prepared three times in the Coating Formulation System.

Table 7. Test Formulations

	Formulation (parts per 100 resin)					
Material	1	2	3	4	5	6
Polymac 57-5776	75	75	75	70	70	70
Resimene 745	25	25	25	30	30	30
pTSA	0.25	0.50	0.75	0.25	0.50	0.75
BYK 300	0.30	0.30	0.30	0.30	0.30	0.30

Coatings were applied to glass panels, cured, then the films removed and thermal properties measured using differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA).

The results are summarized in Table 8. Note that the reproducibility of the coatings made using the combinatorial equipment is very good. In most cases where the error is above 1 percent, one of the three samples is clearly an outlier. This points out the importance of replicates in conducting these experiments. Replicates are required in order to discover bad data points and also determine the statistical significance of the data that is obtained.

Table 8. Thermal Analysis Results

|	DSC Data			DMTA Data		
	Lab	Combi		Lab	Combi	
Formulation	Tg (°C)	Avg. Tg(°C)	% St.Dev.	Tg (°C)	Avg. Tg (°C)	% St.Dev.
1	41.40	38.36	5.89	95.33	95.32	0.02
2	45.80	36.29	1.22	99.93	93.67	3.00
3	44.60	31.10	6.38	--	85.32	0.08
4	41.00	41.10	0.91	105.26	92.00	3.08
5	46.40	36.04	4.42	110.30	90.35	0.10
6	39.00	32.99	0.73	110.26	85.49	0.04

For these experiments the correlation between the lab method and combinatorial method is not high. One reason, we believe, is that the range of data is not very broad. That is, the variation in coating formulation, and therefore the properties is not very wide. The variation in the results does not correlate with the variation in coating formulation very well. More experimentation along these lines is needed. However, this experiment has taught us that the combinatorial system does prepare coatings that are highly reproducible.

Coating Surface Energy System

The coating surface energy system was installed in March 2003. It uses the coating array format that is prepared with the film formation system. Droplets of liquid are placed on the coating, a CCD camera takes a picture of the droplet, and then image analysis is used to determine the contact angle. If liquid droplets of differing surface tension are used, the coating surface energy can be calculated. Currently the system is configured to deposit three droplets of water and three droplets of methylene iodide on the coating surface. The system is shown in Figure 23.
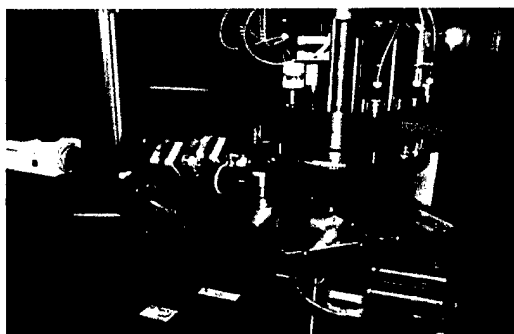
Figure 23. Coating surface energy system.

Use of the surface energy system is just now beginning and some initial data has been described above.

Future Additions to the Facility

The addition of the parallel DMTA and the pull off adhesion test (from Symyx Corp.) will significantly enhance our ability to rapidly screen polymers and coatings for key properties. We are also adding small pieces of equipment to automate operations such as sample purification and work up. In addition, we will also be integrating some existing and off the shelf equipment into the software system.

Combinatorial Bio-assay

For the past 4 months, CNSE has been renovating laboratory space in Dunbar Hall to house the Combinatorial Bio-assay. This facility became functional in July 2003, and will begin to develop combinatorial experimental methods to challenge coatings with bacterial biofilms. One goal of this laboratory to establish correlations between NDSU bio-film fouling / fouling-releaseprotocols and macro-fouling settlement / release observed various field immersion test sites. Another goal is to establish correlations between coating bio-film fouling / fouling-releasecharacteristics and coating mechanical / physical characteristics.

Software

Symyx also supplied a collection of software tools known collectively as Renaissance. The core of the software is the Renaissance Application Server (RAS). The RAS is the central component that interacts with all of the systems and stores library designs as well as screening results in the central Oracle database. The RAS physically resides in the Combinatorial Laboratory.

Library Studio is used to design libraries of materials that are prepared in the Synthesis System or Coating Formulation System. Library designs can be carried out either in mass, mole, or volume units. Composition gradients can be established and special rules can also be used to design material libraries. Statistical designs prepared using Design-Expert can also be imported into Library Studio. A screenshot of Library Studio is in Figure 24.

Impressionist is used to operate the robots used in the Polymer Synthesis, Coating Formulation and Coating Film Formation systems. Impressionist also interacts with **Epoch**, which is the software program that collects data from measurement devices.

Polyview is used to query the database for library designs and experimental results. Data extracted using Polyview can be viewed in the program or it can be exported to another software package such as Spotfire.

Training in each of these packages has been provided by Symyx. Symyx is also available for support and any questions that arise as the software is used.

The importance of this software system cannot be underestimated. Capturing the compositions of each experiment as well as all of the data associated with the experiment is crucial in deriving the maximum benefit from this approach. It is in querying the database and looking for correlations, trends, and relationships that important discoveries are identified. As we move
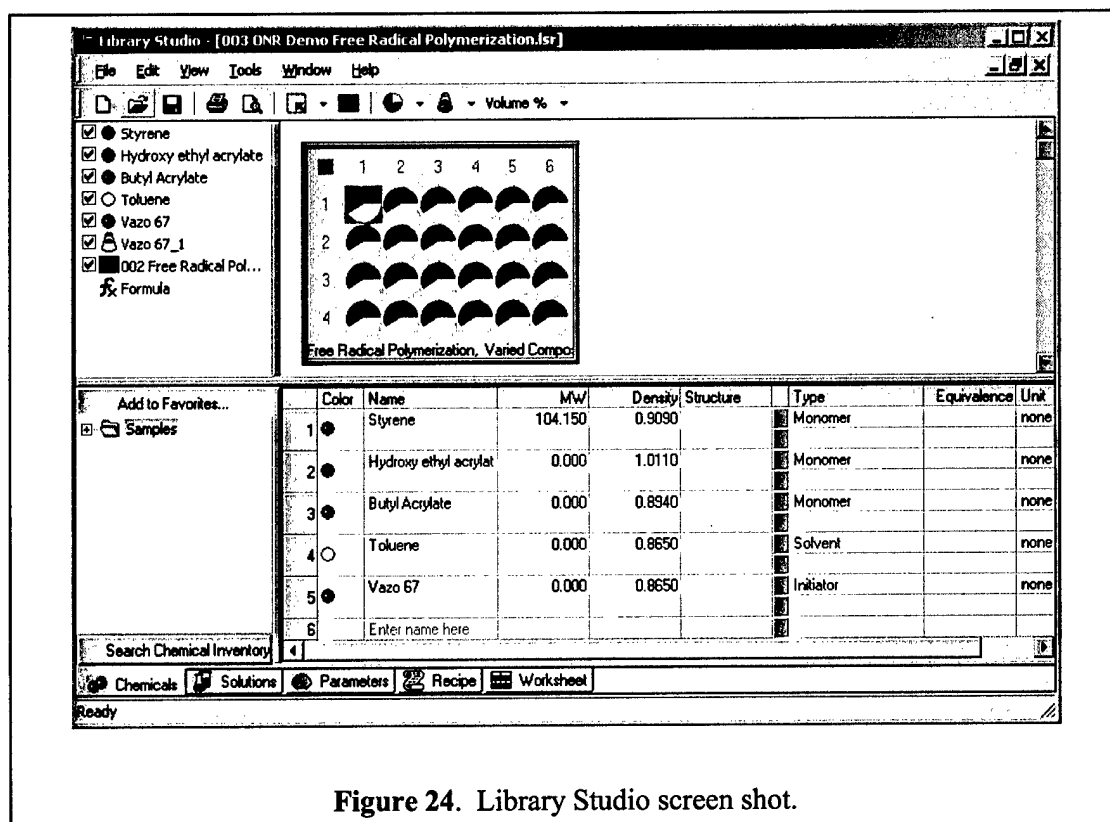
Figure 24. Library Studio screen shot.

forward in the coming year, we will be working with Symyx to develop mechanisms for inserting any and all data generated into the database.

4.0 Program Management

Phase I of this program was managed by Gregory J. McCarthy, Distinguished Professor of Chemistry and Director of the Center for Nanoscale Science and Engineering (CNSE).

Facilities

Research on this program is performed in the Department of Polymers and Coatings, located in the *Research 1* building in the NDSU Research and Technology Park (RTP), and in laboratories on the main campus. The Combinatorial High Throughput (C/HT) experimentation laboratory was established initially in several Dunbar Hall laboratories, pending completion of a new facilities.

A new 75,000 square foot building known as *Research 2*, now under construction in the RTP, will have ca. 4,000 square feet of space dedicated to the new C/HT facility. Completion of construction is planned for March 2004. The equipment from Dunbar Hall will be moved during the summer of 2004.

Personnel

The program began in June 2002 with only the five principal investigators in place. Personnel were hired by CNSE or began graduate work in P&C over the first nine months of work. Their responsibilities and backgrounds are described below.

> **Karen White** is the Manager of Engineering Operations for CNSE. Ms. White earned B.S. and M.S. degrees in Chemical Engineering at the University of Minnesota Duluth and the University of Kentucky, respectively. She worked for five years at the Imation facility in Wahpeton ND, where she worked as a Process and Product Engineer, and advanced to the position of General Supervisor of production. She has extensive experience in statistical Design of Experiments and the qualification of manufacturing tools. She joined CNSE in July 2002.

> **James Bahr** operates the new Combinatorial/High Throughput Experimentation facility in Dunbar Hall, and will be heavily involved in developing new tools during Phase II. He holds a B.S. Degree in Mechanical Engineering from NDSU, and worked for TDA Research Inc. in the Denver area for ten years before joining CNSE in November 2002. With his former employer, he had extensive experience in designing and building laboratory and pilot-scale automated systems for NASA, DOE and DoD clients.

> **Shane Stafslien** became a CNSE Research Specialist in October 2002. After graduating with a B.S. in Microbiology from NDSU in 1997, he worked as an analytical chemist/scientist for a pharmaceutical testing firm in Fargo, where he supervised biological assays and developed HPLC & LC/MS analytical methods.

> **Eric Christianson** joined CNSE in January 2003. He holds a B.S. degree in Electrical and Computer Engineering from NDSU, and is the analyst and administrator for the database systems of the C/HT software. He had seven years of experience with manufacturing engineering IT and database systems before returning to Fargo.

> **Johnson Thomas** joined CNSE in January 2003 as a Postdoctoral Research Fellow. He received his Ph.D in Polymer Science & Technology from Mahathma Gandhi University, India in 1998. After that worked in the field of Epoxy and UV curable coatings for 2 years in Anabond Ltd. India. He moved on to the National University of Singapore as a Post Doc in 2000 June. While there he developed novel Organic/polymeric materials for Micro Electro Mechanical Systems. Before joining CNSE, he worked as a postdoctoral researcher in University of Bordeaux, France for one year. He also worked in the area of anioic polymerization of vinyl

monomers with Solvay Inc. Dr. Thomas is responsible for the synthesis of novel coating materials with AFFR properties.

David Christianson received a B.A. with majors in Chemistry & Biology from Concordia College in 1999. After college he worked in industry doing bioanalytical pharmaceutical analysis. During that time he amassed 4 years experience with various pieces of high-throughput analytical equipment (HPLC, LC/MS/MS, and GC/MS) and associated sample preparation techniques. Mr. Christianson began work in April 2003. He is responsible for operation, programming, maintenance, and training on C/HT equipment at CNSE.

Because no university has research opportunities and facilities comparable to those available in this program, we are placing special emphasis on training graduate and undergraduate students in the new C/HT methodologies. During Phase I eight students participated in the research program:

Abdullah Ekin and **Partha Majumdar** are P&C graduate research assistants advised by Dr. Webster. Both had had prior experience in polymer synthesis and coating formulation before beginning their studies at NDSU.

Undergraduate Research Assistants **Renae Feldjheim** (Pharmacy), **Daniel Rhomas** (Biotechnology), **Jason Feser** (Microbiology), **Joni Altringer** (Microbiology), **Christy Gallagher-Lein** (Chemistry and Mechanical Engineering), and **Jason Greenwood** (Mechanical Engineering) are working various subtasks in the program.

Financial

Funding for Phase I was $3,307,000. The bulk of our funding was assigned to capital equipment need to develop the C/HT capability The approximate breakdown of expenditures was: 79% C/HT tools; 11% personnel; 4% operating; 6% indirect costs.

The program will continue into a second phase. Phase II began on 01-May-03 with funding of $4,455,000 to cover work through 30-Jun-04. The emphasis on capabilities-building continues; 60% of the Phase II budget is assigned to C/HT capital acquisitions and facilities improvements.

Information Transfer

The five principal investigators participated in the ONR program review and the *International Congress on Marine Corrosion and Fouling*, in San Diego during July 2002.

As of the close of Phase I, there had been no presentations of papers or submission of manuscripts for this new program. Presentations and submissions based on first year results are scheduled for Phase II.